A STUDY OF THE STRENGTHENING OF GLASS BY IONIC DIFFUSION

A THESIS

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A STUDY OF THE STRENGTHENING OF GLASS

BY IONIC DIFFUSION

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SUMMARY

A typical soft glass (Kimble Type R-6) containing 68.0 weight per cent SiO_2, 15.5 weight per cent Na_2O, 11.5 weight per cent MgO, BaO, CaO, and 5.0 weight per cent minor oxides was chosen as the base glass. Several techniques were used to exchange K^{+1} and/or Li^{+1} ions for Na^{+1} ions near the surface of glass rods. Depending on the temperature used, relative to the strain point of the glass, both Li^{+1} for Na^{+1} and K^{+1} for Na^{+1} can result in the formation of a compressive layer on the surface of the glass. Since glass always breaks in tension, this layer of compressive forces will substantially increase the net effective strength of the glass.

For Li^{+1} - Na^{+1} ion exchange, a variety of lithium salts were used, and the effects of time, temperature, and surface condition were studied, using both molten salt baths and spraying techniques. In all cases where measurable Li^{+1} - Na^{+1} ion exchange took place, severe surface cracking and decomposition resulted. Thus no net strength increases were possible.

The best results were obtained using K^{+1} - Na^{+1} ion exchange. The optimum temperature for treatment was determined to be about 750°F. Leaching glass rods in molten KNO_3 salt baths at this temperature resulted in strength increases

of as much as 167 per cent for four hours of heat treatment. Spraying saturated aqueous solutions of KNO_3 on the surface of rods followed by heat treatment above the melting point of the salt at 750°F., gave strength increases up to 100 per cent over the "as received" rods.

Techniques giving significant strength increases were considered for possible incorporation into existing production line facilities.

CHAPTER I

INTRODUCTION

Glass, defined as an inorganic material that has been produced by fusion and subsequent cooling, the fused mass becoming rigid without crystallization, is one of the most important products of the ceramic industry today. Its use as a building material, as a container product, and as an ornamental material is increasing year by year. The need for improved methods of strengthening glass becomes more and more critical as the requirements and specifications set by industry, science, and everyday life become more demanding.

The purpose of this study is to explore the chemical strengthening achieved by alkali ion diffusion between the sodium^{+1} ions found in a typical soda-lime glass and other species of monovalent alkali ions brought into contact with the surface of such glass during heat treatment. The effects of tempertture, time, and species and concentration of foreign alkali ions were investigated. The more promising techniques of strengthening soda-lime glass found were investigated as to possible incorporation in existing production line facilities.

CHAPTER II

REVIEW OF THE LITERATURE

Introduction

Glass has a combination of desirable properties which constitute a unique asset for many modern-day needs when compared to other available materials (1). These include:

1) Transparency
2) Hardness
3) Good durability
4) Low cost
5) Relative light weight
6) Ease of forming
7) Nondeformability.

One drawback in using glass for many applications, however, is its lack of strength.

The low strength of glass is caused by the inability to be plastically deformed at low temperatures. Since there is no plastic flow at ambient temperatures, there can be no ductile elongation to dissipate stresses or grain boundaries to stop crack propagation (2). A minute surface flaw, under relatively low stresses, can initiate cracks which propagate to failure. In metals and other crystalline solids, plastic flow takes place due to imperfections in the crystal

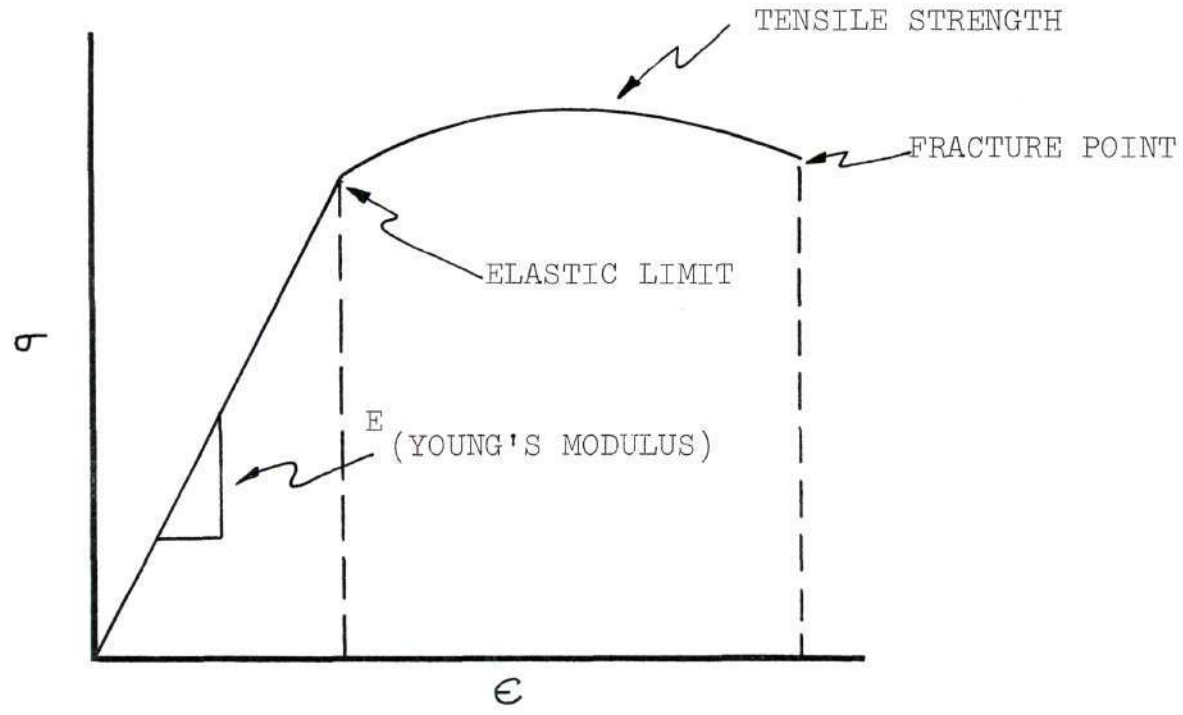
lattice causing slip and twinning. Since glass is a non-crystalline solid, no such long range lattice defects occur. Once the elastic limit has been exceeded, glass will break with no measurable sign of plastic flow. Stress-strain curves shown in Figure 1 are typical of a crystalline solid, such as metal, and a non-crystalline solid such as glass (3).

From studies (1) of inter-atomic forces, backed up by strengths obtained on fibers drawn under almost ideal laboratory conditions, an intrinsic strength of about two million pounds per square inch is possible for glass; however, surface flaws markedly reduce this strength, often to less than one per cent of this value.

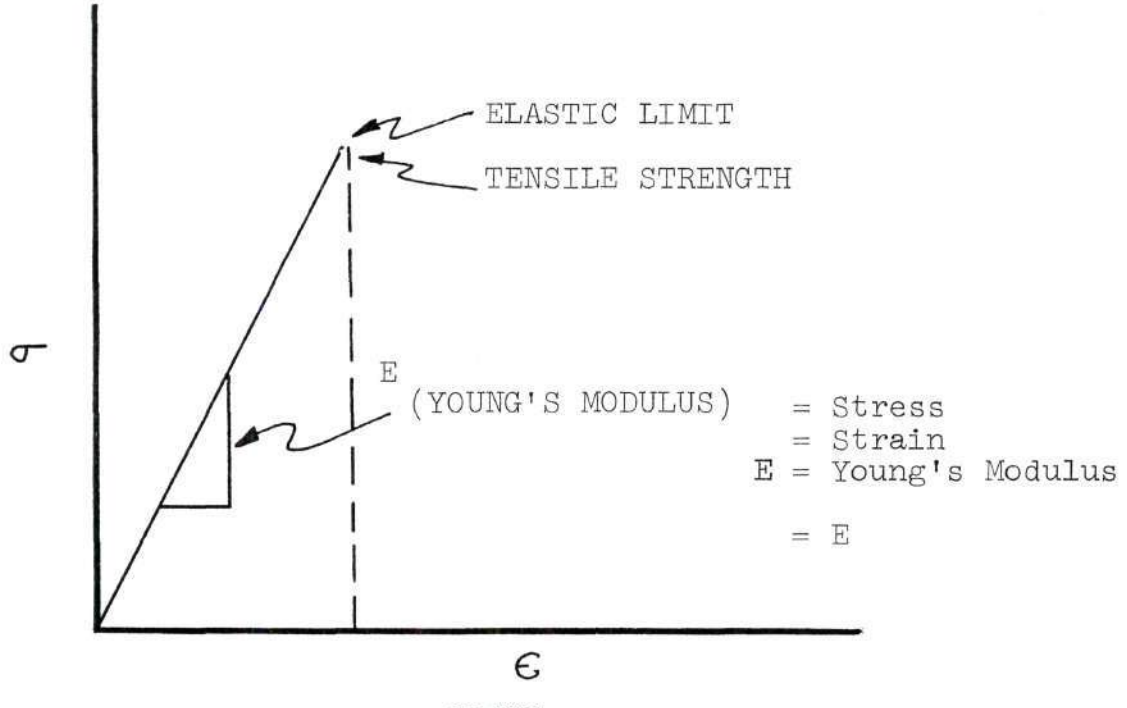
Surface flaws in glass are caused in several ways:

1) A critical gradient in temperature when a glass is cooled in the soft state during molding, annealing, and/or tempering.
2) Surfaces in contact with dies, molds, and extruders during fabrication.
3) Abrasion.
4) The effects of moist air, water, gases, and chemicals in contact with the surfaces of the glass.

Several techniques for increasing the strength of glass will be covered in the following discussion. The most promising appears to be ion exchange, whereby monovalent,



CRYSTALLINE SOLID



GLASS

Figure 1. Stress-Strain Curves for Crystalline Solids and Glass.

alkali ions present in the glass are replaced by other monovalent, alkali ions having a different atomic size. Under certain conditions this will result in the formation of compressive forces on the surface of the glass. Several methods of obtaining ion exchange will be discussed along with the theory and structural analysis of exchange mechanisms.

Techniques and Properties of Ion Exchange

The several methods of strengthening glass depend on one of two mechanisms (1). First, surface flaws may be removed from the glass. This in itself is useless unless the surface is then protected from further abrasion and/or contact with the atmosphere.

In the second method, compressive forces are induced in the surface of the glass. When ordinary glass cools, the surface cools first since it is in direct contact with the surrounding air at lower temperature. As it rapidly cools, it solidifies and forms a shell around the uncooled glass inside. It also contracts and plastically deforms the hot interior. Later, as the inside glass cools, it shrinks, thus putting compressive forces on the surface. This condition results, to some extent, when glass of any composition cools. In ordinary applications, glass never breaks in compression, but always in tension. Therefore, in order to cause failure in glass having a surface layer in

compression, enough force must be applied to not only exceed the elastic limit of the bulk glass, but also to overcome the compressive forces on the surface. If the thickness of the compressive surface layer or the magnitude of the compressive forces in the layer can be increased, the glass can be greatly strengthened. As long as this layer of compressive forces is not penetrated by scratching, abrasion, or reaction with the environment, the glass remains strong.

Several techniques are available to achieve a layer of compressive forces on the surface. They differ in feasibility of application and in maximum strength increase possible. (Articles having sharp re-entrant angles cannot be physically tempered since these sharp angles will serve as weak spots, but they can be chemically tempered. Also, physical tempering produces strength increases limited to about 25,000 pounds per square inch, while chemical strengthening can yield increases of well over 100,000 pounds per square inch [4].) These strengthening techniques range from thermal tempering, based solely on heat treatment and cooling rate for the bulk glass, to chemical treatment in which the composition of the surface layer is altered. This may be done by coating the bulk glass with a second glass composition having a lower coefficient of thermal expansion. On cooling, even under almost equilibrium conditions, the bulk glass will contract more than the surface layer, therefore putting the surface in compression. Of course

the thickness of the secondary glass coating and the compositional differences between the bulk and surface glass can be used to control both the thickness and magnitude of the compressive layer.

Another way of obtaining strength increases for two-phase glasses such as the borosilicates, involves the selective etching away of one phase to the desired depth. Additional heat treatment to collapse the etched portion and fill the voids leaves the bulk glass unchanged but leaves the surface deficient with respect to one of the two phases. In the case of two-phase borosilicate glasses, etching removes the boron-rich phase from the surface. After heat treatment, the boron-rich bulk glass has a higher coefficient of thermal expansion than the silica-rich surface layer. On cooling, compressive forces will build up at the surface due to the difference in thermal expansion of the different compositions of glass.

A third method results from changing the composition of the glass surface by exchanging cations contained in the bulk glass with other ions having a different ionic size or surface to charge ratio. This is one of the newer and more promising ways of strengthening glass.

In "ion stuffing" or ion exchange, foreign ions, having a different ionic radius from the ions present in the base glass, are diffused into the surface of the glass. If the foreign ions have a larger ionic radius than the alkali

ions present in the base glass and if the diffusion process takes place at a temperature below the strain ponnt of the glass, as they diffuse into the glass surface, they replace smaller ions and are crowded into the existing silicate framework. This crowding of the ionic sites in the glass, as shown in Figure 2, puts compressive forces in the area of exchange. In order to be an effective way of strengthening glass, "ion stuffing" must proceed to a sufficient depth so that abrasion or minute surface cracks will not penetrate the compressive layer.

The strain point of glass is defined as the temperature at which the viscosity of the glass is $10^{14.5}$ poises. Below this temperature, readjustment of the silicon-oxygen structure is very sluggish. Above the strain point for a particular glass composition, the speed at which readjustment proceeds, and therefore at which the glass reaches structural equilibrium, becomes significant.

If the foreign ions have a smaller ionic radius than the ions present in the base glass and the diffusion is carried out above the strain point of the glass, the silicate structure is allowed to readjust and accommodate the smaller ions without allowing stresses to be set up in the layer of exchange. In effect this simply changes the composition of the surface layer. In the case of monovalent alkali ion exchange, the replacement of one alkali species by another alkali species having a smaller ionic radius will, in general,

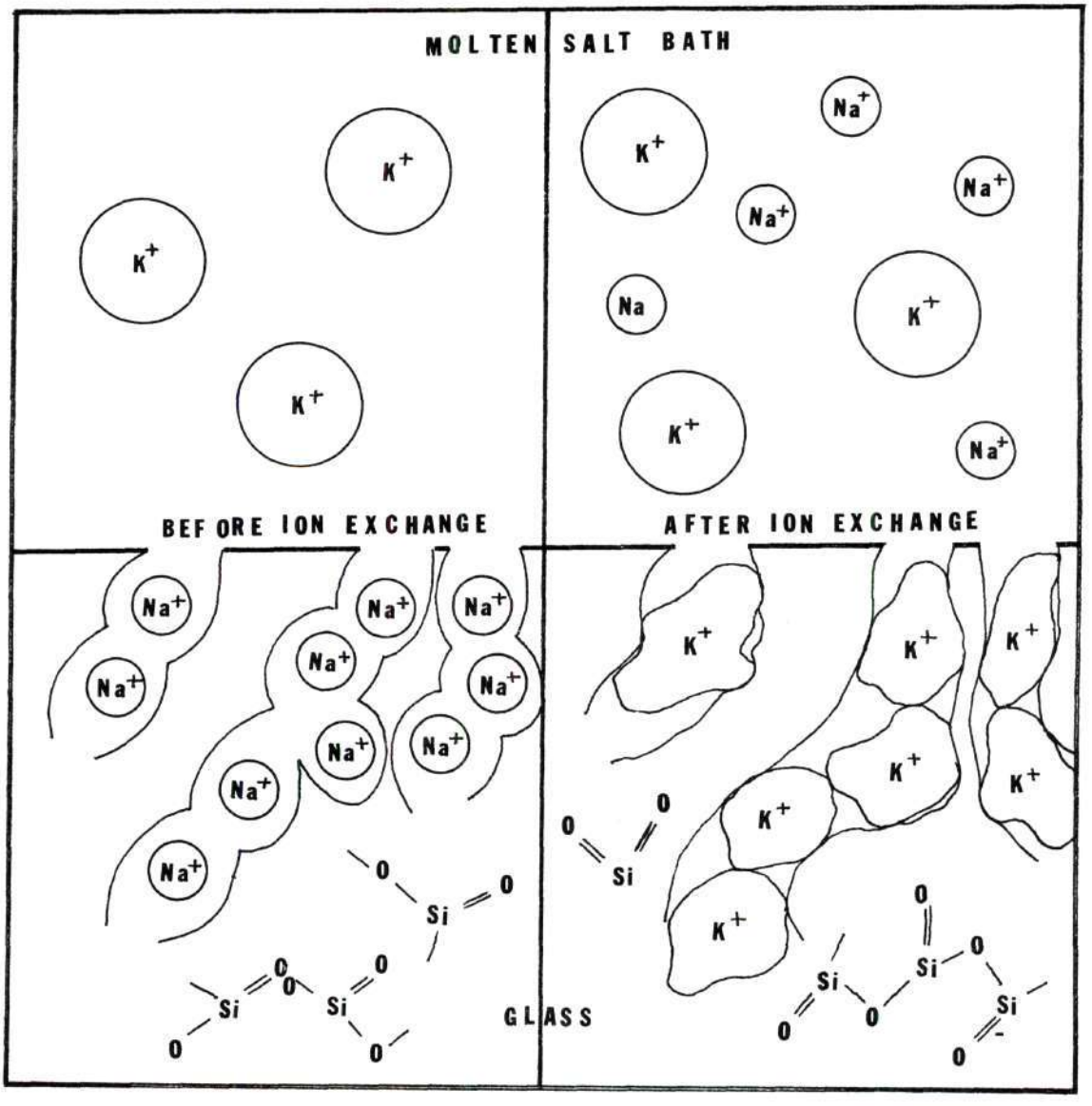


Figure 2. Crowding from Exchange of K^+ for Na^+ Ions in Glass. (After Nordberg(1))

produce a glass having a lower coefficient of thermal expansion. On cooling the glass from above the strain point the interior, large ion rich glass, will contract more than the smaller ion rich surface, again creating a layer of compressive forces on the surface.

In the case where Li^{+1} is exchanged for Na^{+1} in the base glass by immersion in molten lithium salts above the strain point of the glass, further heat treatment can also be employed to crystallize very low thermal expansion, transparent eycryptite crystals on the surface, placing it under very high compressive stress (2).

Crystallization of glasses by controlled heat treatment to form a fine grain structure can also increase strength (2). A nucleating agent is employed to create many small nuclei leading to numerous, fine-grained crystals. These composites may be transparent, and yet crystalline enough to stop crack propagation at grain boundaries. The crystallized glasses, also known as glass-ceramics, can be further strengthened by chemical ion exchange treatments, and these have been shown to possess strengths above 200,000 pounds per square inch even after abrasion and with less variability than with ordinary glass. These glass-ceramics can be made transparent, translucent, or opaque in selected spectral regions, by proper choice of crystal size and composition.

Besides greatly increasing the strength of glass articles, ion exchange also gives another benefit. It has been reported (5) that the chemical durability of glass, having undergone ion exchange, is in many cases, better than that of the base glass. It has been suggested that the leachability of ion-exchanged alkali oxide-alumina-silica glasses decreases due to compressive stresses at the surface.

Structural Analysis of the Ion Exchange Mechanism

According to Kistler (6), silicate glasses consist of an irregular network of silicon and oxygen atoms with very strong and highly directed bonds. Within the structure of this network may also occur certain other atoms such as aluminum which contrast with the silicon atoms in being trivalent and probably possessing bonds which are less strongly directed. Embedded in and surrounded by this very strong and elastic network are monovalent and divalent ions which represent points of mechanical weakness in the structure and the possibility of internal movement, either by migration under the influence of an electrical potential or by diffusion.

At any temperature below the annealing temperature, it is unlikely that a diffusion of atoms in the network structure of silicon, oxygen, and aluminum will take place rapidly enough to produce an equilibrium structure in an

observable time, unless the glass devitrifies. Divalent metallic ions are not known to diffuse at such temperatures, therefore, diffusion in glass is restricted to monovalent metallic ions (6).

Even though diffusion of silicon, oxygen and aluminum ions is greatly restricted below the annealing point, for temperatures above the strain point and approaching the annealing point, internal stresses within the glass are fairly rapidly relieved. This is accomplished as the angles between adjoining silicon-oxygen tetrahedral units sharing a common oxygen atom change without disrupting the individual silicon-oxygen bonds.

When a glass cools from its melt, each alkali ion finds itself encased in a silicate network that conforms to its ionic diameter (6). Any diffusion of these ions must be over strong potential barriers, placed on it by the surrounding network ions and electroneutrality requires that, except for a very few ions per unit volume, each cavity vacated by an ion must shortly be filled by another ion of the same electric charge. Below the strain point, if the only ions present near the vacated site are of a different species, the network will have to stretch if the ion is larger, or be put under tension if the ion is smaller. Above the strain point, the network will readjust to an equilibrium state as diffusion takes place.

Since one ion cannot move into a new position until the ion ahead of it has moved out, the mobility of an ion must be strongly dependent on the other ions in the glass (6). Therefore, both the composition of the glass and the foreign alkali ions introduced into the structure of this glass, effect the rate of diffusion. If a specimen of glass is placed in a mixture of monovalent metallic ions, the diffusion of one of these ion species must depend on the others present. One ion species will always diffuse preferentially.

At high ion concentrations, the paths of diffusion into the glass may become saturated at or near the surface of the glass. When saturation occurs, any increase in the number of available foreign ions will have little or no effect on the rate of diffusion (6).

Since the rate of diffusion is dependent, up to a certain point, on the concentration of the foreign alkali ions available, it is desirable that an excess of these ions be present at all times. Because of this, molten salt baths are often used. Since monovalent ions are always desired and the salts must melt below the strain point of the glass, nitrate salts are usually employed. These salts are melted and the temperature is stabilized to maintain the molten state. Melting points for the alkali nitrates range from 507°F. for lithium nitrate to 633°F. for potassium nitrate (7).

The rate of diffusion is also effected by temperature; however, there are restrictions on the temperatures which can be used (8). Since the success of ionic diffusion strength increases depends on the increase of compressive forces in the surface layer of the glass, the temperatures used must be below the annealing temperatures of the particular base glass where large ions are to be exchanged for smaller ions. If the temperature reaches the annealing range, the forces set up will be almost immediately relieved by a reordering of the network structure. This places a restriction on the melting point of the salt bath. In the case of small ions being exchanged for larger ions in the base glass, the melting point of the salt does not pose such a problem.

When nitrate salt baths are used, the upper limit of temperatures is also set by the thermal stability of the salt (8). The thermal decomposition of alkali nitrates above a certain temperature causes chemical attack to the glass surface.

Since the rate of diffusion approximately follows Fick's Diffusion Law (6), (doubling the depth of diffusion requires a four fold increase in time), the thickness is greatly dictated by time. However, since the layer must be thick enough to protect the glass from abrasion, some type of compromise must be made. It is generally accepted (6), that a thickness of fifty microns is a minimum.

Strengthening by ion exchange can be carried out on ordinary soda-lime glass, using potassium salts. In this process, potassium ions (ionic radius 1.33 Å) replace sodium ions (ionic radius 0.98 Å) in the base glass. It has been generally concluded (6) that the time for diffusion is too long to be practical for typical industrial applications. Time can be decreased by increasing temperature, but a point of diminishing returns results. As at higher temperatures, the silicate structure readjusts faster to relieve stresses.

Fortunately, ion diffusion in other glasses is much higher than in the soda-lime systems. The introduction of alumina greatly speeds up the diffusion process (6). No entirely satisfactory explanation for this has been offered, but Burggraaf and Cornelissen (9) have pointed out that it may have something to do with the well-known effect of alumina in decreasing the number of non-bridging oxygen ions in the network.

Exchanging (6) sodium (ionic radius 0.98 Å) for lithium (ionic radius 0.68 Å) ions is much more effective than exchanging potassium (ionic radius 1.33 Å) for sodium (ionic radius 0.98 Å). This is due to the small ionic sizes involved in the sodium for lithium exchange.

The potassium ion occupies a volume so much larger (about 2.5 times as large) than the sodium ion that if a portion of the sodium ions in a soda-lime glass are replaced

by potassium, a noticeable expansion should occur. Similarly, if lithium replaces sodium (lithium has one-third the volume of sodium), a significant contraction should take place. It is anticipated, then, that exposing a soda-lime glass to a melt of either potassium or lithium salt at a temperature where diffusion can take place should produce very large stresses between the surface of the glass and the interior. Compressive strength of glass is much greater than tensile strength and it can be anticipated that exposure of a soda-lime glass to a potassium salt bath does not destroy a glass as rapidly as exposure to lithium ions. Dipping glass into a lithium nitrate melt for only a few minutes produces a dense white matte surface which microscopic examination shows to be covered by innumerable cracks (10).

Because of cracks on the initial glass surface, micro- and macrodiscontinuities, the exchange of Li^{+1} for Na^{+1} in the glass surface does not proceed homogeneously over the contact phase between glass and melt. Channels and depressions may form in the glass, and in this manner the process of diffusion is enhanced. The formation of depressions causes an increase in the surface area of the glass. On cooling, the glass develops a rough surface with cuts and cohesion cracks (11).

It has been found (1) that the Li^{+1} for Na^{+1} ion exchange takes place so rapidly that there is no problem

in obtaining sufficient compression layer depths in a reasonable amount of time. For example (4), at 400°C., the rate of Na^{+1} - Li^{+1} exchange is about ten times greater than that of K^{+1} - Na^{+1} exchange. Therefore, in order to obtain adequate depth of exchange, an article made of soda-alumina-silica glass must be treated in the molten potassium nitrate at temperatures 100-150°C. higher than the corresponding lithia-alumina-silica glass which is treated in molten sodium nitrate.

The rapid diffusion of Na^{+1} for Li^{+1} and the resulting strength increase, although easily achieved in the laboratory is limited by economic factors for commercial application, except for specialty products, due to the high cost of lithium raw materials relative to sodium batch components.

CHAPTER III

PROCEDURE

Introduction

A typical commercially available container type glass (Kimble Type R-6*) having the composition listed in Table 1, was chosen as a base glass for all experimental work. Samples of this glass were treated by several different ionic exchange methods using both lithium and potassium salts. The following sections will include a description of pre-exchange sample preparation, techniques involving both leaching in molten salt baths and the spraying of aqueous solutions on the surface of glass samples, strength determinations, diffusion studies, and the influence of surface condition on strength.

Pre-Exchange Sample Preparation

As shown in Table 1, type R-6 glass contains approximately 16 weight per cent of exchangeable, monovalent, alkali ions. Some thermal properties of this glass are listed in Table 2.

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*A superior soda-lime glass for laboratory ware, containers and tubing where chemical durability requirements are not strict. Complies with Federal Specification DD-G-541 for Type II glass.

Table 1. Composition of Kimble Flint Glass (Type R-6)

Constituent	% of Composition
SiO_2	68.0%
B_2O_3	1.5%
Al_2O_3	3.0%
BaO	2.0%
CaO	5.5%
MgO	4.0%
Na_2O	15.5%
K_2O	0.5%

Table 2. Physical Properties of Kimble Flint Glass (Type R-6)

Property	Temperature (^{o}F.)
Strain Point	900^{o}
Annealing Point	970^{o}
Softening Point	1290^{o}

In order to insure maximum possible uniformity, a large quantity of this glass in four foot canes, approximately five millimeters in diameter from a single lot was used throughout the experiment. The canes were cut into six inch test specimens and using an oxy-acetylene torch a bead was formed at one end of each rod by which they could be suspended inside a furnace during treatment. Both plain rods and rods with a bead were tested to see if the nonuniform heating used to form the bead had any affect on the strength. It was determined that intense heating of one end of each rod, although causing severe stresses to be set up in the immediate area, had no measurable effect on modulus of rupture values determined from three point loading applied near the center of the rod.

The condition of the surface has a significant effect on the measured strengths of rods broken in this manner. For any strengthening process to be of practical importance (1), it is necessary that the resulting strength be retained during service of the article. For this reason, test rods are usually subjected to scratch or tumble abrasion to simulate actual "in use" conditions prior to determining the strength. Strength values thus obtained are usually lower than those for unabraded samples but with less spread between the individual values than for unabraded samples. What is more important is that these strength values more nearly reflect the glass strength during later use where

abrasion is almost certain to occur. The majority of rods tested in this investigation were not subjected to such standard abrasion, but no special precautions were made in handling the rods either before or after treatment. It can therefore be assumed that the rods were subjected to normal abrasion through contact with adjacent rods and apparatus, and through contact with the atmosphere, water, and handling.

No effort was made to improve the glass surface prior to treatment for the majority of rods. It is assumed that if any of the techniques discussed in this paper were incorporated into production line facilities, treatment would be given to rods soon after fabrication and which had virgin surfaces. This might change the magnitude of strength increases reported here, but it should not seriously alter any trends noted.

A sample group of 25 "as received" rods was broken using three point loading on an Instron Universal Test Machine and the modulus of rupture was determined for each rod. This group served as a standard for comparison with later groups of treated rods.

Molten Salt Baths

Following examples found in the literature, a variety of treatments were tried in which sample groups of rods were leached in molten salt baths. Rods were suspended by their head from a 304 stainless steel place which had holes drilled

in it and submerged in a one liter stainless steel beaker containing the molten salt bath. The rods were leached at severaltemperatures for varying lengths of time in a variety of potassium and lithium salts. In some cases, surface attach was so rapid and severe that tests were discontinued after a short period of time. In other cases, strength increases were noted and tests were continued up to as long as 15 hours. The salt bath compositions and experimental conditions for these experiments are summarized in Table 3. A detailed discussion of the particular temperatures, times of leaching, and the particular salts used will be found in the results section. Some properties (7) of the various salts used are given in Table 4.

An electric globar furnace was used throughout the experiment. A chromel-alumel thermocouple was connected to a Leeds and Northrup strip-chart recorder for continuous temperature monitoring. The thermocouple was sealed inside a borosilicate glass tube to protect it from the salt vapors. The recorder was checked periodically with a potentiometer to insure accurate temperature measurement. The furnace reached equilibrium quickly and the temperature remained essentially constant $\pm$ 10^{o}F. over indefinite periods of time.

During all experiments, the beaker was first filled with salt crystals and heated until melting took place. Additional salt was then added to fill the beaker to within

Table 3. Experimental Time, Temperature and Compositions Investigated for Leaching in Molten Salt Baths.

Salt Bath Composition	Temperature (°F.)	Time (Minutes)				
KNO_3	675	120	240	360	480	720
KNO_3	825	120	240	360	480	720
KNO_3	1000	120	240	360	480	-
KNO_3	750	240	-	-	-	-
$LiNO_3$	600	150				
$LiNO_3$	1000	1	2	5		
$LiNO_3 + KHSO_4$	(See Appendix E)					
50% $LiNO_3$ + 50% $NaNO_3$	745	2				
50% $LiNO_3$ + 50% $NaNO_3$	540	12				
50% $LiNO_3$ + 50% $NaNO_3$	435	5	10	20	30	
50% $NiNO_3$ + 50% $NaNO_3$	405	10	20	30		
LiCL	1150	5	10			
50% LiCl + 50% $NaNO_3$	650	5				

Table 3. Continued

Salt Bath Composition	Temperature (°F.)	Time (Minutes)				
50% LiCl + 50% $NaSO_4$	800	5				
5% $LiNO_3$ + 95% $NaNO_3$	350	5	10	20		
10% $LiNO_3$ + 90% $NaNO_3$	350	5	10	20		
5% $LiNO_3$ + 95% NH_4NO_3	310	20				
10% $LiNO_3$ + 90% NH_4NO_3	310	20	45	60	75	90
25% $LiNO_3$ + 75% NH_4NO_3	310	18	36	54	72	90
50% $LiNO_3$ + 50% NH_4NO_3	335	18	36	60	75	
75% $LiNO_3$ + 25% NH_4NO_3	445	18	36	54		
60% $LiNO_3$ + 40% NH_4NO_3	400	30	60	120	240	900

Table 4. Properties of Various Salts Used

Salt	Melting Point (°C.)	Melting Point (°F.)	Molecular Weight	Density (gms/cc)	Boiling Point (°C.)	Boiling Point (°F.)
Potassium Nitrate (KNO_3)	334	633	111.11	2.11	d* 400	d* 752
Sodium Nitrate ($NaNO_3$)	306.8	584	84.99	2.26	d* 380	d* 716
Lithium Nitrate ($LiNO_3$)	264	507	68.94	2.38	d* 600	d*1112
Lithium Sulfate (Li_2SO_4)	856	1573	109.94	2.22	860	1580
Potassium Bisulfate ($KNSO_4$)	d* 190	d* 374	120.17	-	d* $1/2K_2S_2O_7$ + $1/2\ H_2O$	
Lithium Chloride (LiCl)	614	1137	42.39	2.07	1325	2417
Ammonium Nitrate (NH_4NO_3)	169.6	337	80.04	1.725	210	410
Potassium Pyrosulfate ($K_2S_2O_7$)	300	572	254.33	2.51	d*	d*

*d = decomposes

one inch of the top. In all cases, the molten salt was allowed to reach equilibrium before immersion of the glass rods.

After leaching, the glass rods were removed from the furnace and allowed to air cool. Warm tap water was used to remove salts adhering to the rods. The rods were then rinsed in distilled water and allowed to dry before testing.

Spraying Techniques

During later stages of the research, saturated aqueous solutions of several salts were sprayed on the surface of rods preheated to approximately 300°F. in a small electric furnace. Again the rods were suspended from a stainless steel plate and rotated as a fine mist of the salt solution impinged on the surface. On hitting the hot surface of the rods, the water instantly evaporated, leaving a continuous coating of the salt adhering to the rods.

The coated rods were heat treated at temperatures above the melting points of the various salt coatings. Table 5 summarizes the temperatures, heat treating times, and various salts used in these experiments.

After heat treatment, the rods were removed from the furnace and cleaned using the procedure outlined in the molten salt bath section.

Table 5. Experimental Time, Temperature and Compositions Investigated for Heat Treatment After Spraying With Saturated Aqueous Solutions

Saturated Aqueous Solution	Temperature (°F.)	Time (Minutes)						
$LiNO_3$	600	15	30	30	60			
$LiNO_3$	1050	540						
KNO_3	660	15	30	60	120	240	720	1440
KNO_3	740	15	30	60	120	240	720	1440
KNO_3	800	15	30	60	120	240	720	1440
KNO_3	850	15	30	60	120	240	720	1440
KNO_3	1000	15	30	60	120			

Determination of Strength

All rods were broken on an Instron Universal Testing Machine using a three point loading jig at a crosshead speed of 0.5 cm. per minute and the modulus of rupture calculated using the following equation:

$$M.R. = \frac{8PL}{\pi D^3} \qquad (1)$$

where:

M.R. = Modulus of Rupture in pounds per square inch.

P = Breaking load in pounds.

L = Length of span in inches.

D = Diameter of the rod at the point of fracture.

Rod diameters were measured with standard micrometers measuring to $\pm$ 0.0001 inches. An attempt was made to measure all rods exactly at the point of fracture; however, on fracture, some rods broke in many small pieces and the exact point of breakage was difficult to determine. Several of the "as received" rods were measured at several points and the diameter did not vary more than 0.0005 inches on any one rod. Therefore, for rods not measurable exactly at the break, the error introduced was probably small.

Although all rods were broken in the same manner throughout the experiment, the technique used did not meet the ASTM requirements relating to span length and loading rate. Since relative strength increases or decreases were

all that was desired, this does not pose any serious problem. The reader should keep in mind, however, that the values tabulated in the data should be related to the "as received" standards and not to absolute values for the strength of this type glass which might be available in the literature.

Diffusion Studies

Flame photometry was used to trace the extent of ion exchange for those techniques which produced substantial increases in the modulus of rupture. In this experiment, treated rods were etched in a 12% hydrofluoric acid solution. The depth of the sample removed was determined for each rod by measuring the diameter before etching and noting the weight of the material removed. By removing successive layers of rod and examining for Na^{+1} and Li^{+1} of K^{+1}, it was possible to determine the depth to which exchange was achieved.

Industrial Applications

Throughout the experimental work the primary objective was to develop a technique which could be adapted easily and inexpensively into existing production line facilities. As stated in the literature, it was soon verified that the expense and time involved in strengthening soda-lime glass by replacing the Na^{+1} in the surface layer with K^{+1} would be prohibitive for the majority of high volume production

involving this type of glass. Considerable effort was therefore spent in investigating possible techniques for Li^{+1} ion exchange above the strain point of the glass.

After investing considerable time in experimental techniques for Li^{+1} ion exchange, and gaining only extremely limited success, attention was again focused on K^{+1} ion exchange. The technique of spraying rods with aqueous solutions of potassium salts was a result of this. Although all rods examined earlier in the experiment were sprayed after preheating to 300°F., an investigation was made to determine the maximum allowable preheat temperature to see if this technique could be applied to objects cooled in a lehr.

A limited effort was also made to look at strength increases possible using this technique on a glass having a virgin surface. Glass rods were treated for three minutes in a solution of 42 per cent by volume of HF, 50 per cent by volume H_2SO_4, and 8 per cent by volume H_2O. After removal from the etching solution, some of the rods were rinsed in distilled water and immediately tested for modulus of rupture determination with a minimum of handling. Another group of rods was rinsed, preheated to the maximum allowable temperature, and sprayed with a saturated solution of potassium nitrate. These rods were then heat treated under conditions of temperature and time which gave maximum strength increases, as determined through earlier

experimentation.

After heat treatment, half of the rods were tested for modulus of rupture. The remaining half, along with an equal number of "as received" rods were abraded for thirty seconds by rolling the rods over a piece of glass coated with 120 grit silicon carbide. The two groups were then broken and the modulus of rupture determined. This was used to determine the magnitude of residual strength increase for the group of rods having undergone potassium^{+1} ion diffusion.

CHAPTER IV

RESULTS AND DISCUSSION

The primary objective of this research was to study methods of strengthening a typical soda-lime glass through the exchange of monovalent, alkali ions at or near the surface of the glass. The exchange of both K^{+1} and Li^{+1} for the Na^{+1} present in the soda-lime glass composition was investigated using primarily two techniques. The first of these involved leaching the glass rods in a variety of molten potassium and lithium salt baths. Also, saturated aqueous solutions of several salts were sprayed on the surface of rods and the rods were heat treated above the melting points of these salts. The effect of these treatments on the strength of glass rods was evaluated by three point modulus of rupture determination. A discussion of techniques and results will follow.

The combined results of these studies were used in considering the potential of ion exchange as a means of strengthening soda-lime glass articles in existing production line facilities.

Ion Exchange Using Molten Salt Baths

Initially, a sample group of twenty-five "as received" rods was broken and the modulus of rupture was determined for each rod. These results are listed in Appendix A. The average modulus of rupture for this group of rods was 21,600 pounds per square inch. This value was used throughout the investigation as a basis on which to compare treated rods. (It should be noted that this value does not agree with values found in the literature for this type of glass. This is due to the fact that ASTM procedures were not followed in breaking the rods. Reference is made to the procedure section where the technique for breaking rods is discussed.)

Potassium Ion Exchange

The first series of experiments was run using pure molten potassium nitrate (KNO_3) as the salt bath. Sample groups of approximately 20 rods each were leached from two hours to twelve hours in baths at 675°F., 825°F., and 1000°F. The average modulus of rupture for each of these combinations is given in Table 6 and is shown graphically in Figure 3. Tabulated data for the individual rods in each group is given in Appendix B, Table 12.

The rods leached in KNO_3 at 675°F. became stronger with increasing leaching time, up to the maximum tested time (12 hours). This increase in strength was most rapid during the initial four hours and then slowed down. Assuming that for relatively thin surface layers, the

Table 6. Average Room Temperature Modulus of Rupture (Pounds per Square Inch) for Soda-Lime Glass Rods Leached in Molten KNO_3.

Leaching Time (Hours)	Leaching Temperature (°F.)		
	675	825	1000
0	21,600	21,600	21,600
2	34,400	54,800	44,700
4	45,800	55,500	31,400
6	49,900	54,000	18,000
8	56,500	53,800	25,500
12	61,300	53,300	---

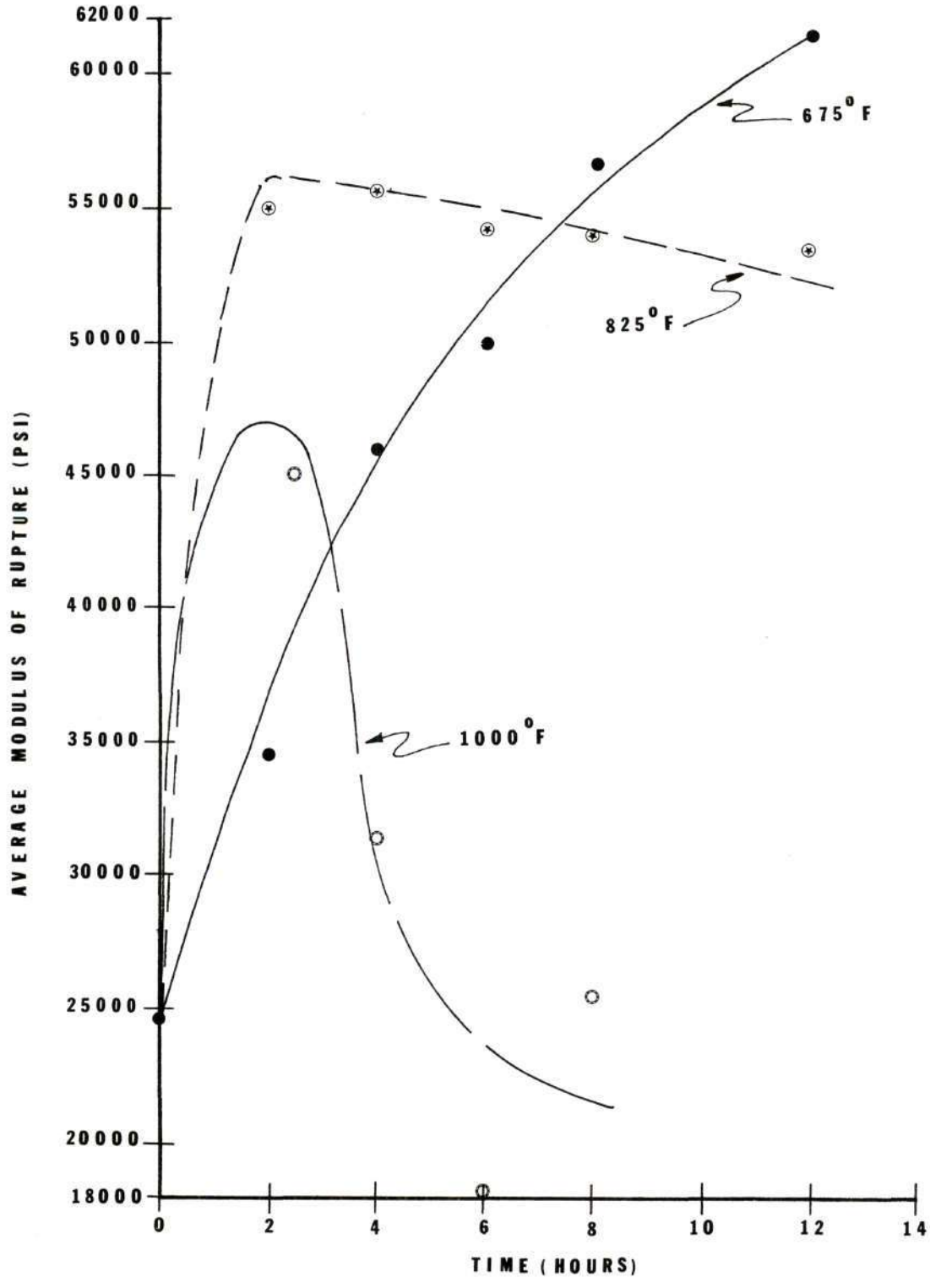


Figure 3. Average Modulus of Rupture as a Function of Time for Soft Glass Rods Leached in KNO_3 at 675°, 825°, and 1000°F.

increase in strength is directly proportional to the thickness of the layer of K^{+1} ion exchange, then according to Fick's Law of Diffusion, in order to double the strength increase the leaching time would have to be multiplied by a factor of four. From Table 6, it can be seen that the strength increased about 11,000 pounds per square inch for the two hour period from two to four hours of leaching at 675°F. The increase in strength during the next eight hour period was about 14,000 pounds per square inch. When the magnitude of the calculated standard deviation of these measurements is taken into account, the above assumption (that strength increase is directly proportional to the thickness of exchange as explained by the Fick model) gives a reasonable estimate of the relation between strength increase and time, at least during early stages of the diffusion process.

Table 6 shows that the rods leached in KNO_3 at 825°F. underwent a large strength increase of about 33,000 pounds per square inch during the first two hours. However, at four hours the strength had leveled off and was decreased slightly thereafter. This is probably the result of two independent effects. At this elevated temperature, approaching the strain point of the glass, compressive forces built up at the surface of the glass are certainly going to be gradually relieved by a reorientation of bond angles within the glass structure. Eventually an equilibrium will be

between compressive forces built up through diffusion and the relieving of these forces by internal atomic movement. It should also be noted that about 752°F., KNO_3 begins decomposing into oxides which cause surface attack. This would counteract strength increases due to ion diffusion.

At 1000°F. there was initially a moderate strength increase, but this was quickly offset by surface attack from decomposition products.

The results suggested an optimum temperature for K^{+1} ion exchange would be between 675 and 825°F. A temperature of 750°F. was selected to verify this. This temperature is just below the decomposition point for KNO_3 and therefore the highest temperature at which strength increases resulting from ion diffusion would not be at least partially offset by surface attack. These results are tabulated in Appendix B, Table 13. The rods treated for four hours at 750°F had an average modulus of rupture of 57,600 pounds per square inch. This represents a 167 per cent increase in strength over the "as received" rods. The only time-temperature combination tested which gave a larger strength increase was at 675°F. and here twelve hours of leaching were required instead of four to reach the same level of average strength.

Flame photometry was used to measure the change in alkali content in molten KNO_3 at 750°F. to determine the depth and degree of diffusion of potassium^{+1} ions into the

glass rods. The data collected is given in Table 7.

Table 7 shows that 97.9 per cent of the monovalent alkali ions present in the base glass are sodium^{+1} and 2.1 per cent are potassium^{+1}. For rods leached 15 minutes and 2 hours only limited exchange took place and this was essentially confined to the outermost 10 microns of the surface. For rods leached for 20 hours, considerable exchange was noted. Fifty per cent of the sodium^{+1} ions were replaced by potassium^{+1} in the outer 11 microns of surface. Significant exchange extended down to a depth of about 20 microns but below 20 microns, little increase in the amount of potassium^{+1} was found.

Lithium Ion Exchange

A pure lithium nitrate bath was used in an attempt to exchange lithium^{+1} ions for sodium^{+1} ions in the base glass. Initially a bath temperature of 1000°F. was used since treatment above the annealing point of the glass was desired. At this temperature, extreme surface attack was evident after only five minutes of leaching. Preheating the rods to 1000°F. and immediately transferring them to the bath, also at 1000°F., failed to reduce the attack. Examination of the surface of rods treated in this manner, using both reflected light and scanning electron microscopes, revealed severe surface attack, Figure 4. A cross sectional view of a rod leached in lithium nitrate at 1000°F. for 12 hours, Figure 5, shows that the attack extends at least a millimeter into the glass

Table 7. Flame Photometry for Rods Leached in Molten KNO_3 at 750°F.

Time of Leach	Surface Layer Analyzed	Per Cent of Total Monovalent, Alkali Ions Present	
		$\%Na^{+1}$	$\%K^{+1}$
"As Received" (No Leach)	0-22 Microns	97.9	2.1
15 Minutes	0-11 Microns	96.3	3.7
	11-36 Microns	97.6	2.4
	36-49 Microns	97.7	2.3
2 Hours	0-7 Microns	95.2	4.8
	7-16 Microns	97.2	2.8
	16-28 Microns	97.5	2.5
	28-51 Microns	97.7	2.3
20 Hours	0-11 Microns	48.4	51.6
	11-19 Microns	88.4	11.6
	19-44 Microns	97.5	2.5

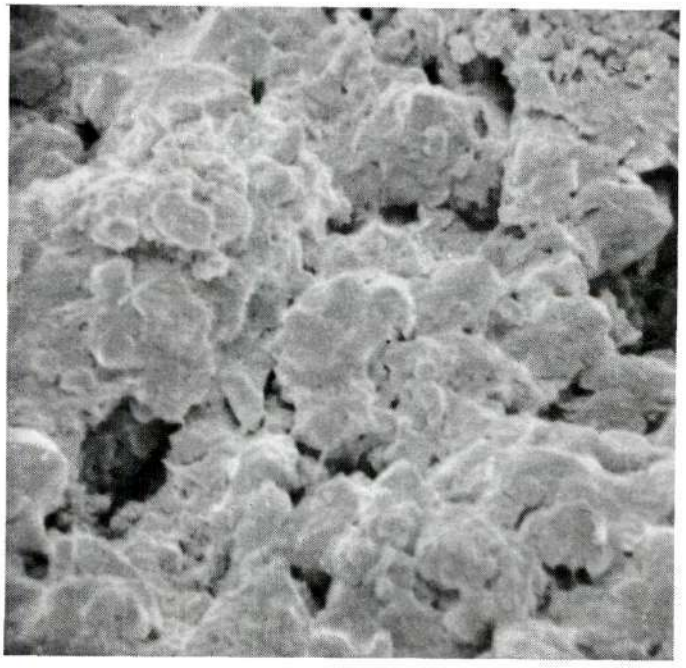


Figure 4. Scanning Electron Micrograph Showing Surface Attack of Soda-Lime Glass Leached in $LiNO_3$ at 1000°F. for 5 Minutes (X5000).

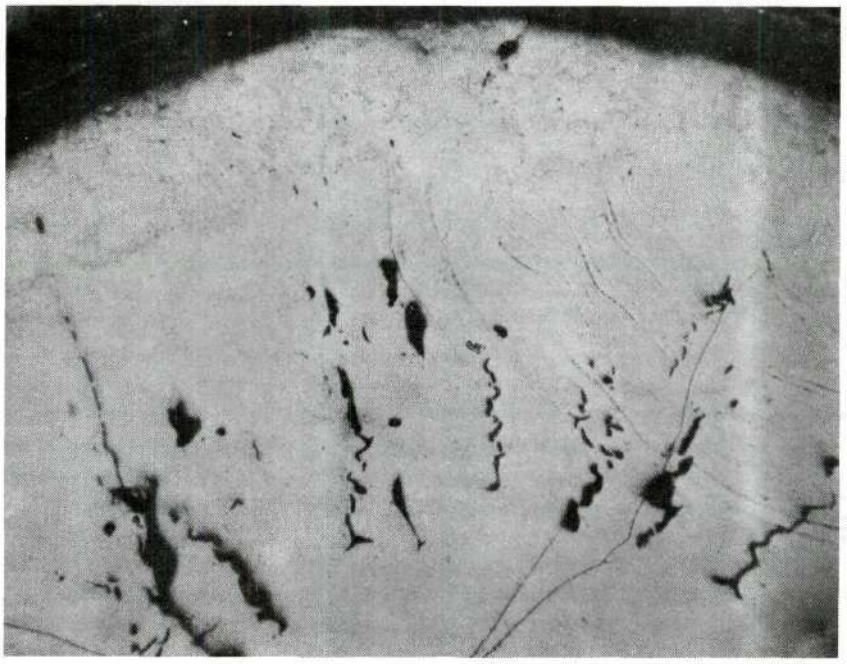


Figure 5. Photomicrograph Showing a Cross Section of Soda-Lime Glass Rod Leached in $LiNO_3$ at 1000°F for 12 Hours (X60).

rod.

X-ray powder diffraction showed the presence of several lithium silicate and silica phases in attacked surfaces. It is interesting to note that the primary phases found were $Li_2Si_2O_5$ and α-cristobalite. Although β-eucriptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) was mentioned in the literature as a primary devitrification product on the surface of glass leached in $LiNO_3$, none was detected. It is assumed that this is due to the limited amount of aluminum present in the base glass.

Flame photometry analysis of samples leached in $LiNO_3$ showed that as far down into the glass as cracking and devitrification occurred, essentially 100 per cent of the sodium^{+1} present in the base glass had been replaced by lithium^{+1}.

Etching the glass rods in a combination of hydrofluoric and sulfuric acids prior to heat treatment in contact with molten $LiNO_3$ failed to reduce surface attack. It was hoped that acid etching would improve the glass surface enough to prevent uneven ion exchange from causing surface attack. Evidently this is not possible, since removing as much as 0.5 millimeter of the surface failed to prevent rapid and severe attack.

Mixed Alkali Ion Exchange

Several experiments were run with mixtures of $LiNO_3$ and $NaNO_3$ to see what effect reducing the lithium

concentration would have on surface attack. It was hoped that the presence of large amounts of $NaNO_3$ in the bath would slow the diffusion process down to the extent that the surface attack could be avoided. A 50 per cent $LiNO_3$ and 50 per cent $NaNO_3$ salt bath was first tried. At 405°F. there was no surface attack visible under the reflected light microscope after 10 minutes of leaching. After 20 minutes small areas of surface attack became evident. At 30 minutes, a fairly complete pattern of cracks covered the surface of the rods. As the temperature of the bath was increased, the attack became significantly more rapid and severe. At 540°F., there was well-developed surface attack after 12 minutes of leaching. At 745°F., only two minutes were required to produce severe attack. This agrees with the results of Botvinkin and Denisenko (11) who found that the surface cracking evidently occurs on cooling the glass, due to unequal diffusion rates around surface cracks and imperfections, and for a given degree of exchange, is not effected by the composition of the salt bath. Using baths containing 5 weight per cent $LiNO_3$ and 95 weight per cent $NaNO_3$, and exposing rods for only 5 minutes at 350°F. caused noticeable surface attack and great decrease in the modulus of rupture compared to the as received rods.

Several other combinations of alkali salts were used in forming molten salt baths for leaching. All combinations tried, except for those involving NH_4NO_3, a discussion of

which will follow, caused varying degrees of surface attack after short periods of exposure to glass rods. A discussion of these studies is summarized in Appendix C.

A series of experiments was carried out using NH_4NO_3 and $LiNO_3$ baths. The NH_4NO_3 was used to lower the melting point of the bath to see if surface attack could be prevented by leaching at lower temperatures. Rods were leached in a 5 weight per cent $LiNO_3$ - 95 weight per cent NH_4NO_3 solution for twenty minutes at 310°F. and no attack resulted. For a 10 weight per cent $LiNO_3$ - 90 weight per cent NH_4NO_3 solution at 310°F., no attack was noted after 1.5 hours of leaching. Rods treated in 25 weight per cent $LiNO_3$ - 75 weight per cent NH_4NO_3 and 50 weight per cent $LiNO_3$ - 50 weight per cent NH_4NO_3 solutions at 335°F. for 1.5 hours showed no attack.

Rods were leached in a 60 weight per cent $LiNO_3$ - 40 weight per cent NH_4NO_3 solution at 405°F. for up to 15 hours and no surface attack occurred on any of the rods submerged in the salt baths. It is interesting to note, however, that certain areas of these rods above the surface of the bath showed significant cracking. It is assumed that the vapor pressure of the $LiNO_3$ is substantially higher at this temperature than that of NH_4NO_3 and it has already been shown that $LiNO_3$ in combination with other salts cause severe surface attack in short periods of time at this temperature.

A sample rod treated in the $LiNO_3$ - NH_4NO_3 bath at

405°F. for 15 hours was analyzed for Li^{+1} ion exchange using atomic absorption. The outer 20 microns contained 11.6 per cent Na^{+1} and 0.0516 per cent Li^{+1}. The outer 175 microns contained 11.2 per cent sodium^{+1} and 0.0103 per cent Li^{+1}. It can be easily shown that the higher percentage of Na^{+1} in the outer 20 microns is due to an excess of sodium^{+1} on the surface of the glass. This indicates that there was little replacement of Li^{+1} for Na^{+1} even after 15 hours of leaching at this temperature and essentially all of the exchange took place in the outer 20 microns. The slow rate of Li^{+1} ion diffusion into this sample was probably due to the low leaching temperature and the large, polarizable NH_4^{+1} ion blocking the paths of diffusion at the surface of the glass.

The NH_4NO_3 salt is very unstable and beging to boil just above 405°F. so increasing the temperature to speed up diffusion was not possible. Thus, at 405°F. the diffusion of lithium^{+1} in $LiNO_3$ - NH_4NO_3 systems is so slow that it would be infeasible even if devitrification and surface cracking could be avoided.

Ion Exchange Using Saturated Aqueous Solutions

An alternative approach for industrial application would be to spray the surface of glass with an aqueous solution of alkali salts and then heat treat the rods above the melting point of the salt. This also appears to be more

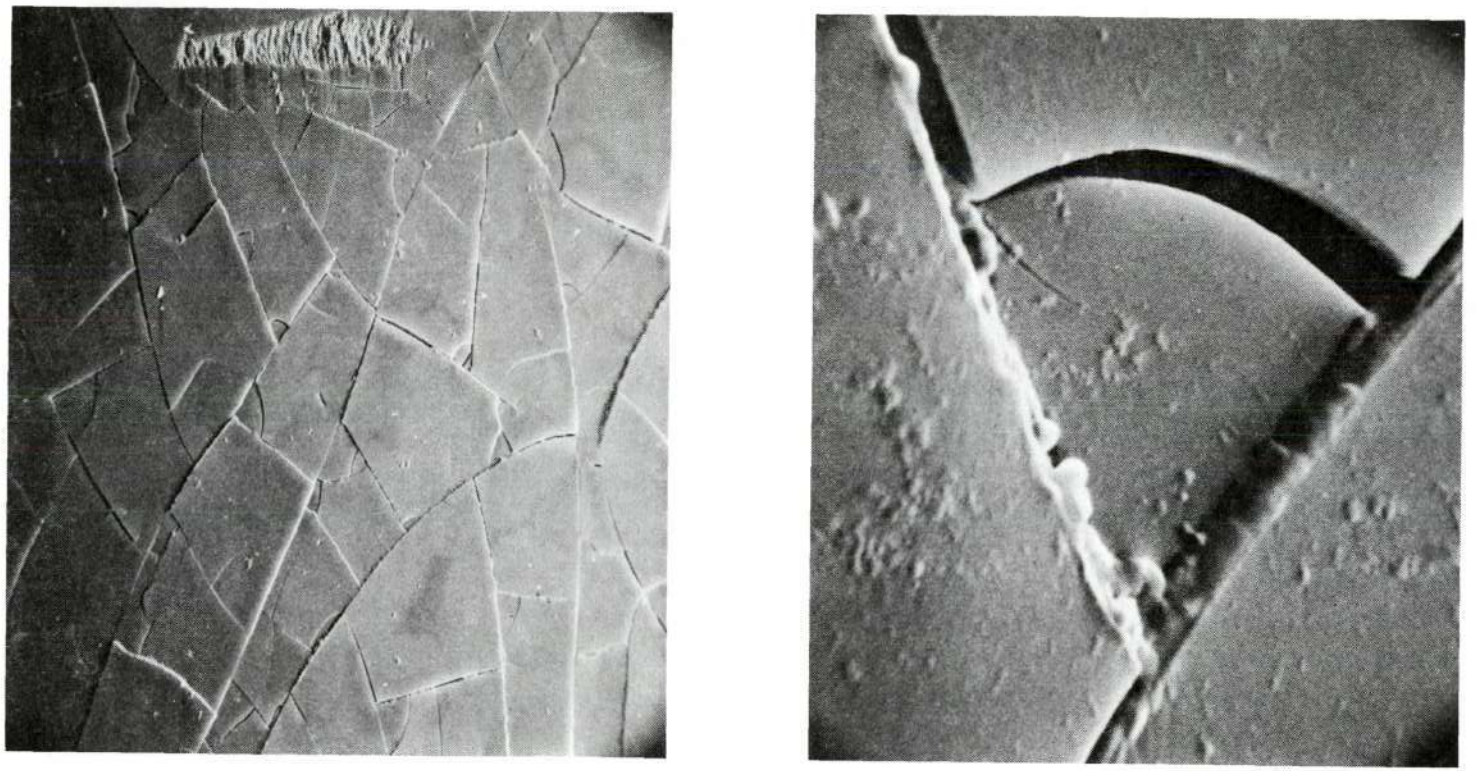
feasible for incorporation into existing production line facilities.

Lithium Ion Exchange

A saturated aqueous solution of $LiNO_3$ was prepared and sprayed on the surface of glass rods preheated to 300°F. in a small electric kiln. On striking the heated surface of the glass rods, the water evaporated leaving a continuous coating of the nitrate salt adhering to the surface of the rods. The coated rods were then transferred to a Globar furnace in equilibrium at 600°F. Severe surface attack was evident on rods heat treated for only two minutes. Scanning electron micrographs, Figure 6, show the crack pattern on the surface of the rods after 15 minutes.

Heat treating such rods well above the strain point failed to improve the surface to any noticeable degree. Further heat treatment to temperatures above the softening point of the glass also failed to improve the surface of the rods. Evidently as the surface of the glass became fluid, the surface cracks were sealed over, thus trapping small amounts of $LiNO_3$ salt inside. Continued heating caused melting and vaporization of these salts which caused the diameter of the rods to increase greatly. After cooling, microscopic examination showed that this was due to a layer of bubbles trapped just below the surface of the glass.

Rods sprayed with an aqueous $LiNO_3$ solution and heat treated at 1050°F., well above the strain point of the glass,



(a) X700 (b) X14,000

Figure 6. Scanning Electron Micrographs Showing Surface Attack of Soda-Lime Glass Rods After Spraying With $LiNO_3$ Solution and Heat Treating for 15 Minutes at 600°F.

also showed surface attack. Evidently this higher temperature only speeded up the attack.

Potassium Ion Exchange

A saturated aqueous solution of KNO_3 was prepared and sprayed on a series of glass rods preheated to 300°F. These rods were heat treated at temperatures ranging from 660°F. to 1000°F. and for times varying from 15 minutes to 24 hours. The modulus of rupture was determined for 20 to 25 rods for each combination of test conditions. These results are tabulated in Appendix D. The average modulus of rupture values are listed in Table 8 and plotted graphically in Figure 7.

The trends found here were closely correlated to those found for rods leached in KNO_3 molten salt baths. The groups heat treated at 660°F. showed increasing strength with time of leaching. The maximum strength obtained over the time span covered occurred at the maximum leaching time (24 hours). This is a strength increase of 38,500 pounds per square inch or an 85 per cent increase over "as received" rods. It can be seen from Figure 7 that nearly 90 per cent of this strength increase had been reached after only four hours. This would seem to indicate that for spraying, after four hours of leaching, the available K^{+1} ions contained in the salt adhering to the surface had been depleted. When an excess of available K^{+1} ions are available, as in the case of large molten salt baths, a large strength increase occurs

Table 8. Average Modulus of Rupture (Pounds per Square Inch) for Soda-Lime Glass Rods Sprayed with a Saturated Aqueous Solution of KNO_3 and then Heat Treated.

Time (Minutes)	Temperature (°F.)				
	660	740	880	850	1000
0	21,600	21,600	21,600	21,600	21,600
15	25,500	30,800	30,700	39,100	26,800
30	27,900	31,900	32,700	36,200	23,800
60	28,900	34,800	39,400	35,900	25,700
120	27,500	37,700	38,800	34,900	20,900
240	35,100	42,500	31,900	32,900	-
720	34,200	42,100	28,800	27,300	-
1440	38,500	41,100	27,400	24,300	-

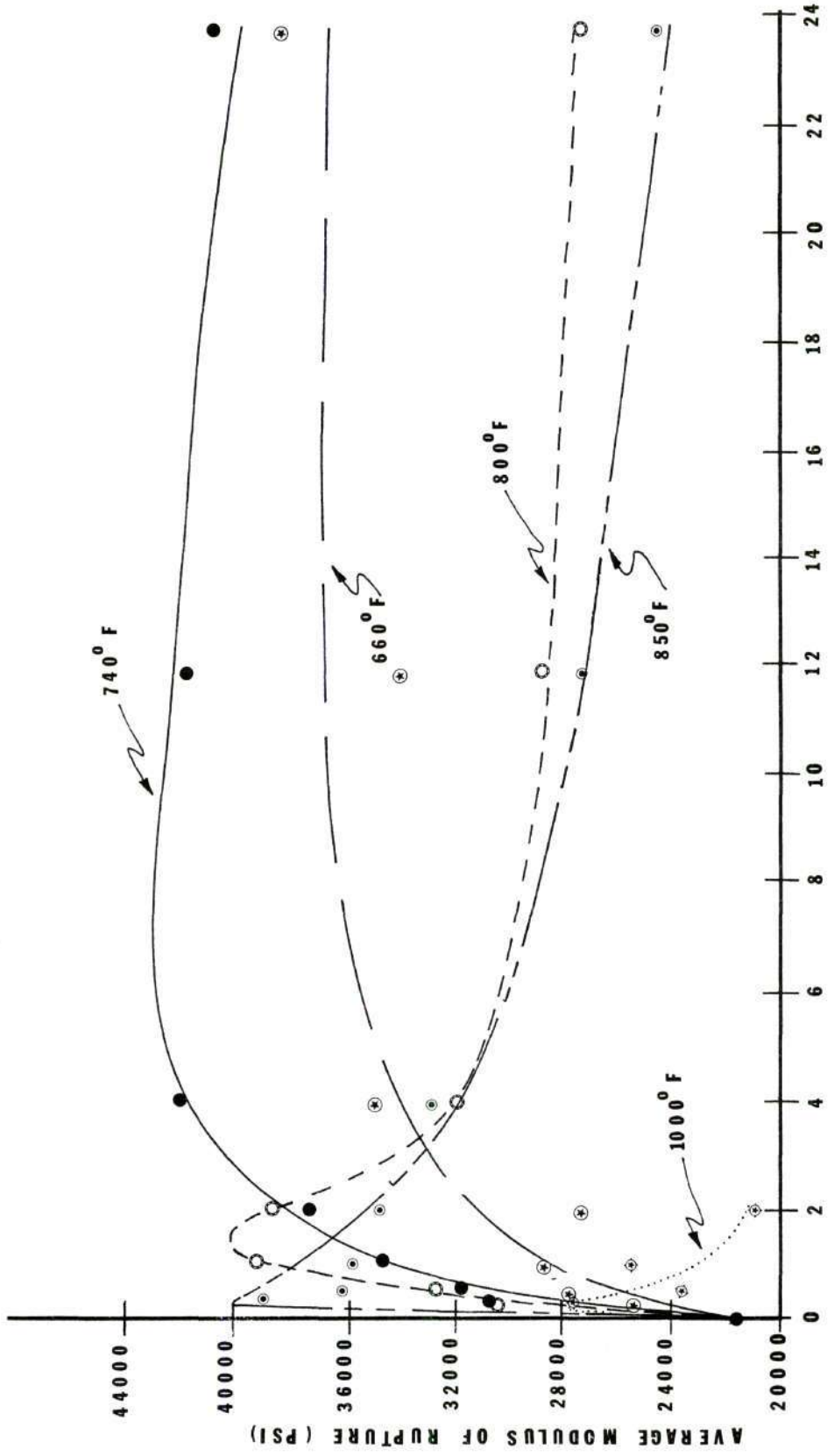


Figure 7. Average Modulus of Rupture As A Function of Time for Soda-Lime Glass Rods Sprayed With a Saturated Solution of KNO_3 and Heat Treated Above M.P. of Salt.

after four hours of leaching (see Figures 3 and 7). Comparing similar temperatures (650°F. vs. 675°F.) at the 12 hour mark, the rods leached in the molten salt bath had more than twice the strength increase shown by those having only the surface coated with KNO_3 salt.

For the rods sprayed with KNO_3 and heat treated at 740°F., the maximum strength increase occurred after four hours. The average strength of 42,500 pounds per square inch represents approximately a 100 per cent strength increase over "as received" rods. For heat treating times greater than four hours, Figure 7 shows a slight decrease in average strength values. This decrease could easily be due to normal statistical variations. Standard deviations calculated for groups in this region are around 7,000 pounds per square inch. Since 740°F. is below the decomposition temperature for KNO_3, this decrease in strength cannot be attributed to surface attack by decomposition products; however, it could be due partially to readjustment of atomic positions in the structure, thus relieving some of the stress between surface and interior.

Rods treated at 800°F. showed a maximum strength after one hour and for those treated at 850°F. after only 15 minutes. At neither of these temperatures, did the maximum average strength reach that obtained for rods treated at 740°F. At this point, temperatures were above the decomposition temperatures for the KNO_3 salt and the limited

strength increase can be explained by the countereffect of surface attack.

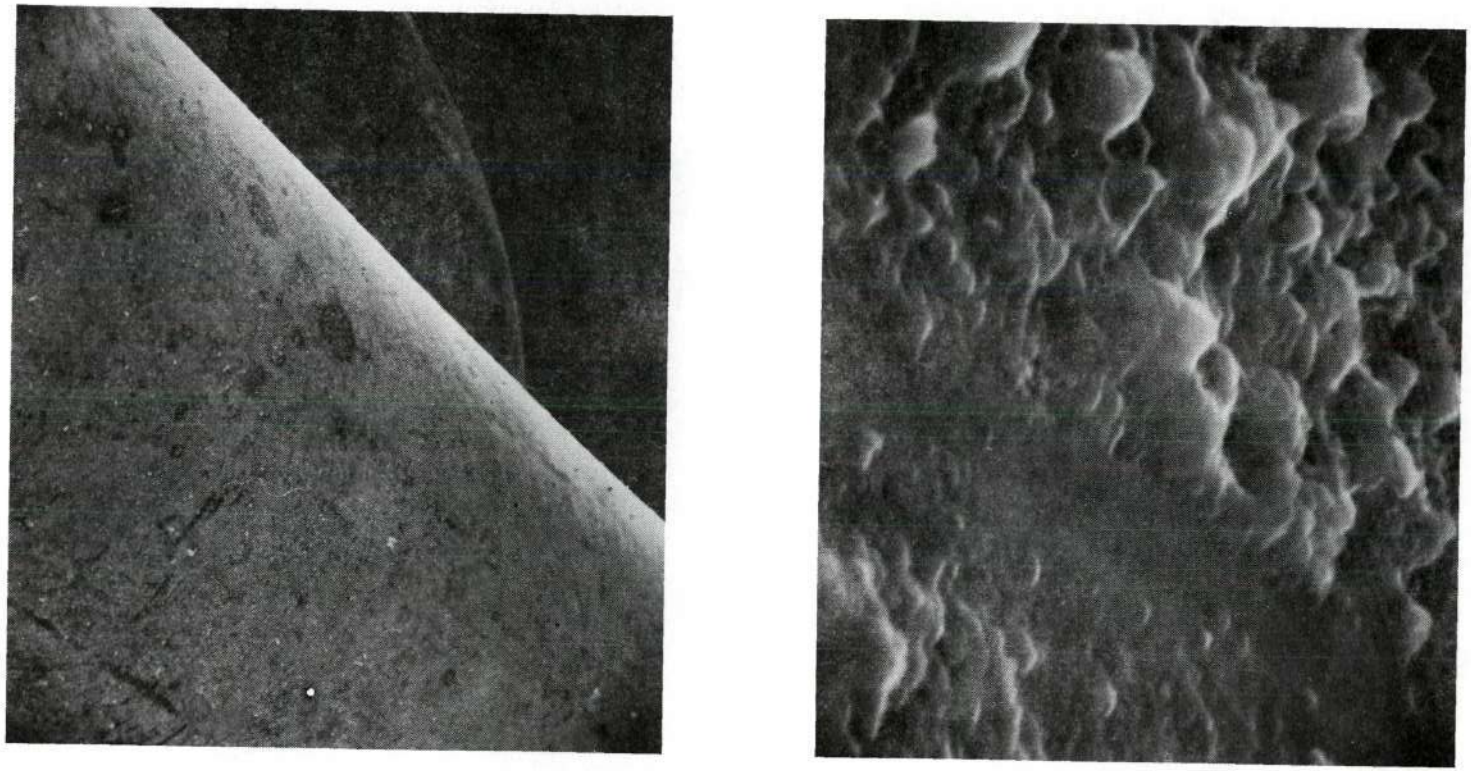
Here again, the maximum average strength for sprayed rods was only half that for rods leached in a molten KNO_3 salt bath. It can be seen that the rate of strength increase during the initial hour of treatment was very similar for sprayed and leached rods (see Figures 3 and 7). From this and other comparisons, it appears that surface attack by decomposition products is more prevalent in the vapor phase than in the liquid. The nitrates have rather high vapor pressures at elevated temperatures and treatment above 752°F. for extended periods of time probably reduces the amount of salt adhering to the surface of the rods substantially. After 12 hours of heat treatment, the average strength of rods sprayed with KNO_3 and treated at 800°F. had dropped to approximately 28,000 pounds per square inch or only slightly above the "as received" strength (Figure 7). For rods leached in KNO_3 molten salt baths, after 12 hours, the strength had dropped only slightly to 53,000 pounds per square inch (Figure 3).

For rods treated at 1000°F. strength increases reached a maximum almost instantly and then rapidly dropped off to below the "as received" strength (Figure 7). Here, not only was the temperature above the strain point of the glass, but surface attack was plainly evident after one hour

of treatment. To verify this attack by the vapor phase, a group of "as received", unsprayed rods were suspended above a KNO_3 molten salt bath, but not in contact with it, and treated at 1000°F. After only one hour of treatment, removal from the furnace, cooling, and washing, the rods were covered with a dense white matte coating, similar in appearance to the rods attacked by $LiNO_3$. Figure 8 shows scanning electron micrographs of the surface of one of these rods.

It again appears that a temperature of approximately 750°F. would be optimum for treating rods sprayed with an aqueous solution of KNO_3. This is the maximum temperature possible, therefore allowing maximum diffusion rates, without exceeding the thermal decomposition temperature of the KNO_3 salt.

Flame photometry studies run on rods sprayed with KNO_3 and heat treated at 750°F. are summarized in Table 9. This table shows that although some exchange did take place in rods heat treated for 15 minutes and 2 hours, it was confined to the outer 10 microns of surface. For rods heat treated for 20 hours, there is evidence that exchange occurred at least to a depth of 25 microns, to some limited degree, but probably not to the extent required to develop significant compression of the surface. The high sodium^{+1} content of the outer 10 microns of rods heat treated for 20 hours remains an anomoly and no explanation can be offered.



(a) X25

(b) X12,300

Figure 8. Scanning Electron Micrographs of Surface Attack for Soda-Lime Glass Rods Suspended Above Molten KNO_3 at 1000°F. for 1 Hour.

Table 9. Flame Photometry Data for Rods Sprayed with KNO_3 and Heat Treated at 750°F.

Time of Leach	Surface Layer Analyzed	Per Cent of Total Monovalent, Alkali Ions Present	
		$\%Na^{+1}$	$\%K^{+1}$
15 Minutes	0-8 Microns	93.7	6.3
	8-17 Microns	97.5	2.5
	17-64 Microns	97.6	2.4
2 Hours	0-10 Microns	91.1	8.9
	10-25 Microns	97.2	2.8
	25-48 Microns	97.9	2.1
20 Hours	0-11 Microns	97.9	2.1
	11-25 Microns	96.5	3.5
	25-40 Microns	96.8	3.2
	40-63 Microns	97.6	2.4

Industrial Applications of Ion Diffusion For Strengthening Soda-Lime Glass

After extensive experimentation, no acceptable method of Li^{+1} ion exchange was found for strengthening soda-lime glass. Evidently, as stated in the literature, large amounts of Al_2O_3 are required in a soda-lime glass to prevent surface attack during the Na^{+1} - Li^{+1} ion exchange. Therefore, this discussion will be limited to Na^{+1} - K^{+1} exchange.

For exchange using KNO_3 salt, whether sprayed on the glass surface or melted to form a molten salt bath, 750°F. appears to be the optimum temperature for treatment. The depth of exchange was determined using diffusion studies where flame photometry was used to measure the change in alkali content of the glass. These studies showed that treatments using molten salt baths gave a much thicker layer of diffusion than when salt was sprayed on the surface of the glass, and heat treated above the melting point of the salt. Therefore, increased or more extensive compressive forces are present on the surface of soda-lime glass leached in molten salt baths. Of course the thicker layer of compression is desirable since, if abrasion from subsequent handling penetrates the layer in which exchange has taken place, its effect is nullified. However, the great cost of containing and maintaining large molten salt baths for treatment will probably remain intolerable for any but limited and specialized production items.

Therefore, the approach of applying KNO_3 to glass surfaces by spraying, followed by heat treatment at elevated temperatures, above the melting point of the salt and approaching the temperature at which thermal decomposition takes place may be the only economically feasible technique. To further evaluate this technique, an effort was made to determine the maximum temperature at which the rods could be preheated before spraying with the saturated aqueous solution of KNO_3 without causing thermal cracking of the glass due to the temperature gradient between the interior and surface of the rod. Obviously this would depend on the size, shape, and wall thickness of the glass body being sprayed and therefore it is impossible to assign a single quantitative number. For the 5 millimeter rods used in this study, a temperature of about 550°F. appeared to be the maximum. For thicker walled objects and for those less symmetrical in shape, the maximum temperature would obviously be less than 550°F.

From the above study it can be seen that if the KNO_3 was sprayed on the surface during cooling in a lehr in a typical production line facility, the rods would have to be reheated to a higher temperature in order to speed up the rate of diffusion to a reasonable level.

One approach to increase the temperature at which the KNO_3 is applied would be to find a carrier for the KNO_3 with a lower heat of vaporization than water. This would

slow down the heat loss from the surface of the glass, and thus increase the temperature at which the KNO_3 could be applied without causing thermal shock.

If the KNO_3 were sprayed on glass during the cooling process, it is assumed that the surface condition might be considerably better than for the rods tested in this study. Some surface imperfections would be present due to thermal gradients between surface and interior during fabrication and from contact with dies, molds, or extruders, but abrasion and contamination from atmospheric gases, probably the cause of a majority of serious surface flaws, would be extremely limited.

To test the possible effects of surface condition on strengths attainable and depth of diffusion, a group of rods were etched in a hydrofluoric-sulfuric acid solution. The rods were placed in the acid and gently agitated for 30 seconds, removed, and the acid washed off with distilled water. Measurements showed that approximately 200 microns were removed from the glass surface. Half the etched rods were immediately heated to 550°F. and sprayed with a KNO_3 solution. These rods were then heat treated at 750°F. for four hours.

Five rods, etched but not sprayed, were tested and their modulus of ruptures determined. Five other rods, etched but not sprayed, were abraded using 120 grit silicon carbide. The silicon carbide was spread over the surface of

a large glass sheet, wet, and the rods rolled over the surface using a tilting and rocking motion for 30 seconds. These rods were also tested and their modulus of ruptures determined.

After heat treatment the remaining rods were divided into two groups. Five rods were broken and five others were abraded in the manner described above and then broken. These results are tabulated in Appendix E and summarized in Table 10. This table shows that the strength increase of the acid-etched rods was about 62 per cent over the "as received" rods. The rods sprayed and heat treated at 750°F. showed a strength increase of 125 per cent (see Table 10) or slightly better than rods not acid-etched and treated for four hours at 740°F. and shown in Figure 7. However, for the abraded rods, the strengths of both groups were reduced to the same level, and well below the strengths of "as received" rods.

Perhaps the abrasion treatment these rods were exposed to exceeded the abuse they would have received from handling and exposure to the atmosphere, but in any case, the compressive forces developed during heat treatment offered no improved resistance to abrasion over the untreated rods. This indicates the compressive layer was not deep enough to resist penetration during abrasion.

Since the thickness of the layer in which exchange took place was limited, an effort was made to determine

Table 10. Average Modulus of Rupture Values for Acid-Etched Soda-Lime Glass Rods Treated with KNO_3 at 750°F. for 4 Hours and Abraded

Treatment	Average Modulus of Rupture (Pounds Per Square Inch)
"As Received" Rods (No Treatment)	21,600
"As Received" Rods Acid Etched for 30 Seconds	35,000
"As Received" Rods Acid-Etched for 30 Seconds and Abraded with 120 Grit Silicon Carbide	16,700
"As Received" Rods Acid-Etched for 30 Seconds, Sprayed with KNO_3, and Heat Treated for 2 Hours at 750°F.	48,600
"As Received" Rods Acid-Etched for 30 Seconds, Sprayed with KNO_3, Heat Treated for 2 Hours at 750°F., and Abraded	15,600

whether or not the available K^{+1} ions were exhausted from the salt deposited on the glass surface. The salt remaining on the surface of a rod heat treated for four hours at 750°F. was removed and flame photometry was used to determine the ratio of alkali ion species in the salt. This analysis showed that the salt contained a Na^{+1} - K^{+1} ratio of only 0.11. The Na^{+1} - K^{+1} ratio which started at zero, increased during heat treatment. This would cause the rate of K^{+1} ion diffusion into the glass to decrease somewhat. However, with almost 90 per cent of the available monovalent, alkali ions remaining in the salt being K^{+1}, there is no indication that equilibrium had been reached after 4 hours. Evidently, there is no transport mechanism available to carry the Na^{+1} ions away from the glass surface in the rods sprayed with a thin coating of KNO_3 as there is in the large molten salt bath. This would cause a build-up of Na^{+1} ions at the surface of the glass thus greatly interferring with K^{+1} ion diffusion into the glass.

Theoretical calculations shown in Appendix F, show that the maximum thickness of diffusion for the average amount of KNO_3 sprayed on the surface of a glass rod was 40.6 microns. Since it is doubtful that all the available K^{+1} diffused into the glass and since the literature reported that a minimum of 50 microns were required, the results reported above are not surprising. Total exchange is certainly not required in order to build up a compressive

layer and for partial or incomplete exchange, the depth of diffusion could theoretically exceed 50 microns. Flame photometry studies showed that the layer of diffusion for treatment at this temperature and time was only approximately 10 to 15 microns.

If the amount of K^{+1} contained in the coating of KNO_3 initially deposited on the glass is insufficient to generate a compressive layer thick enough to resist penetration, or if a build-up of Na^{+1} ions on the surface of the glass interferes with the diffusion process, the only alternative would be to repeat the spraying, followed by additional heat treatment in cycles, until a layer of sufficient thickness was reached. This would obviously be out of the question for commercial use unless a technique was developed for spraying the salt on the surface of the glass at or near 750°F. without causing thermal shock. Even if this were the case, the disadvantages of using a molten salt bath would soon be exceeded.

In conclusion, the prospects of strengthening soda-lime glass having a composition similar to the one tested in this study seem remote, at least as an economical addition to existing production line facilities. Several avenues of study not covered in this investigation which could lead to exchange techniques with commercial potential include:

1) Slight modifications of glass composition, resulting in an increased Al_2O_3 content and

therefore improving the possibility of Li^{+1} ion exchange.

2) The use of other potassium salts with higher thermal stabilities allowing heat treatment at higher temperatures.

3) The use of an electrical potential to speed up K^{+1} ion diffusion after spraying the potassium salt on the surface.

4) Spraying the heated rods with molten KNO_3 rather than an aqueous solution of the nitrate salt.

5) Treat in molten salt baths at elevated pressure to increase decomposition temperature and therefore heat treatment temperature.

6) Try an Al^{+3} - Li^{+1} salt combination.

CHAPTER V

CONCLUSIONS

1. For K^{+1} ion exchange in soda-lime glass, using KNO_3 salts, the optimum temperature to use was found to be 750°F. This is the maximum temperature possible before decomposition of the KNO_3 salts cause surface attack which, at least partially, offsets further strength increases due to ion exchange.

2. The largest strength increase found for soda-lime glass rods leached in molten KNO_3 salt was 167 per cent which occurred after four hours of heat treatment at 750°F.

3. For rods leached in molten KNO_3 salt baths at 750°F., approximately 20 hours were required for the thickness of the layer of ion exchange to approach 50 microns.

4. Spraying soda-lime glass rods with a saturated aqueous solution of KNO_3 followed by heat treatment at temperatures above the melting point of the nitrate, but below the temperature at which decomposition of the salt occurs, resulted in strength increases of as much as 100 per cent over the "as received" strength.

5. When rods were sprayed with aqueous solutions of KNO_3 and heat treated, even after 2 hours at 750°F., exchange was limited to the outer 10 microns.

6. For rods sprayed with aqueous solutions of KNO_3 and heat treated at 750°F., abrasion of the surface reduced the strength to a level equivalent to that of "as received" rods abraded in the same manner. This indicates that the layer in which ion exchange took place was so thin that it was easily penetrated by the abrasion.

7. No suitable technique was found for exchanging a significant amount of Li^{+1} for Na^{+1} ions in soda-lime glass which did not severely attack the surface of the glass.

APPENDICES

APPENDIX A

DETERMINATION OF THE "AS RECEIVED" STRENGTH FOR SODA-LIME GLASS RODS

In order to determine the effectiveness of various strengthening techniques, twenty-five "as received" rods were broken using three point loading on an Instron Universal Test Machine and the modulus of rupture calculated for each rod. These results, the average modulus of rupture, and the standard deviation are given in Table 11.

Table 11. Modulus of Rupture Values Determined for "As Received" Rods

Rod Number	Load (Pounds)	Diameter (Inches)	Modulus of Rupture (Pounds per Square Inch)
1	35.2	0.2009	22,200
2	37.1	0.1996	23,800
3	30.8	0.1992	19,900
4	31.9	0.1981	20,900
5	18.3	0.1996	11,700
6	32.6	0.1992	21,000
7	37.8	0.1961	25,600
8	29.9	0.1989	19,400
9	33.6	0.2010	21,100
10	37.1	0.1964	25,000
11	32.6	0.2029	19,900
12	40.5	0.1988	26,300
13	32.6	0.2005	20,600
14	27.5	0.1959	18,600
15	44.5	0.2003	28,300
16	32.4	0.1988	21,000
17	26.0	0.1983	17,100
18	31.0	0.1971	20,600
19	31.5	0.1983	20,600
20	37.7	0.2000	24,000
21	23.2	0.1954	15,900
22	38.0	0.1992	24,500
23	42.9	0.1957	29,200
24	33.4	0.1981	22,000
25	31.9	0.1995	20,500
		Average Modulus of Rupture =	21,600
		Standard Deviation =	3,800

APPENDIX B

DETERMINATION OF STRENGTH FOR SODA-LIME GLASS RODS LEACHED IN MOLTEN KNO_3 BATHS

Sample groups of about twenty glass rods were leached in 100 per cent potassium nitrate molten salt baths at temperatures of 675°F., 825°F., and 1000°F. for times ranging from two to twelve hours. The modulus of rupture for the rods, along with an average modulus and standard deviation for each group, is tabulated in Table 12.

Analysis of this data indicated that the optimum temperature for treatment would be around 750°F. Table 13 gives the data obtained for a group of ten rods leached in KNO_3 for 4 hours at 750°F.

Table 12. Modulus of Rupture of Soda-Lime Glass Rods Leached in KNO_3 at a) 675°F for 2 Hours

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1990	36.4	29,500
2	0.1989	40.1	32,500
3	0.1990	50.5	40,900
4	0.2024	39.1	30,100
5	0.2007	42.8	33,800
6	0.1978	37.3	30,800
7	0.2003	45.1	35,800
8	0.2005	45.4	35,900
9	0.2018	40.8	31,700
10	0.1994	25.3	20,400
11	0.1993	42.4	34,200
12	0.1990	52.4	42,500
13	0.2017	38.7	30,100
14	0.2003	69.5	55,200
15	0.1992	41.0	33,100
16	0.1969	43.6	36,500
17	0.1999	37.7	30,100
18	0.2017	57.2	44,500
19	0.2000	31.7	25,300
		Average Modulus of Rupture =	34,400
		Standard Deviation =	7,400

Table 12. Continued. b) 675°F. for 4 Hours Leaching

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1999	86.4	69,100
2	0.1997	45.2	36,200
3	0.2013	49.1	38,400
4	0.2005	68.1	53,900
5	0.2038	43.3	32,600
6	0.2010	89.9	70,700
7	0.2055	45.6	33,500
8	0.1987	66.7	54,300
9	0.2032	58.4	44,400
10	0.1979	59.3	48,800
11	0.2003	44.4	35,200
12	0.1978	69.7	50,100
13	0.2028	73.9	56,500
14	0.2056	42.8	31,400
15	0.1993	43.1	34,800
16	0.2012	53.0	41,500
17	0.1976	47.2	39,000
18	0.1945	80.1	69,400
19	0.1983	54.4	44,500
20	0.2016	41.7	32,500
		Average Modulus of Rupture =	45,800
		Standard Deviation =	12,500

Table 12. Continued. c) 675°F. for 6 Hours Leaching

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1999	66.9	53,400
2	0.2034	56.8	43,100
3	0.1948	65.8	56,800
4	0.2002	71.8	57,100
5	0.2005	77.6	61,400
6	0.1994	45.9	37,000
7	0.2008	65.0	51,300
8	0.1965	83.4	70,200
9	0.1987	67.4	54,800
10	0.2035	79.0	59,800
11	0.2030	40.0	30,500
12	0.2005	59.5	47,100
13	0.2006	79.4	62,700
14	0.1977	37.8	31,200
15	0.1999	56.8	45,400
16	0.2059	69.0	50,400
17	0.1983	52.4	42,900
18	0.1997	53.2	42,600
		Average Modulus of Rupture =	49,900
		Standard Deviation =	10,600

Table 12. Continued. d) 675°F. for 8 Hours Leaching

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1940	44.5	38,900
2	0.1980	61.6	50,600
3	0.1957	73.9	62,900
4	0.1979	74.3	61,100
5	0.1961	64.1	54,200
6	0.2005	35.2	37,900
7	0.2014	84.3	65,800
8	0.1985	83.4	68,100
9	0.1974	71.5	59,200
10	0.2000	79.9	63,700
11	0.1980	84.7	69,600
12	0.2042	88.7	66,500
13	0.1968	60.2	50,400
14	0.2051	53.7	39,700
15	0.2001	71.8	57,200
16	0.2007	83.8	66,100
17	0.1985	70.8	57,700
		Average Modulus of Rupture =	56,500
		Standard Deviation =	11,400

Table 12. Continued. e) 675°F. for 12 Hours Leaching

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
L	0.1940	69.0	60,300
2	0.2051	87.3	64,600
3	0.2017	99.8	77,600
4	0.1984	78.0	63,700
5	0.2047	84.5	62,800
6	0.1958	52.1	44,300
7	0.1994	68.8	55,400
8	0.1991	77.8	62,900
9	0.1959	75.0	63,600
10	0.2047	57.2	42,600
11	0.2011	86.9	68,200
12	0.2025	89.6	68,800
13	0.1967	75.7	63,500
14	0.1969	75.9	63,400
15	0.1959	79.0	67,100
16	0.1983	64.1	52,400
		Average Modulus of Rupture =	61,300
		Standard Deviation =	8,600

Table 12. Continued. f) 825°F. for 2 Hours Leaching.

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1965	41.5	34,900
2	0.2005	64.6	41,100
3	0.1996	65.3	52,400
4	0.1972	74.1	61,700
5	0.2002	58.4	46,500
6	0.1966	54.0	45,400
7	0.1971	58.3	48,500
8	0.2022	68.8	53,100
9	0.1999	60.5	48,400
10	0.2023	82.0	63,200
11	0.2015	84.0	65,500
12	0.1989	65.3	52,900
13	0.2020	95.0	73,600
14	0.2032	92.2	70,100
15	0.1978	60.0	49,500
16	0.2006	75.5	59,700
17	0.1968	83.9	69,400
18	0.1969	84.3	41,000
19	0.1991	64.8	52,400
20	0.2003	70.8	56,200
		Average Modulus of Rupture =	54,800
		Standard Deviation =	9,900

Table 12. Continued. g) 825°F. for 4 Hours Leaching.

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1981	64.1	52,600
2	0.1978	67.2	55,400
3	0.1969	62.5	52,200
4	0.2019	79.6	61,700
5	0.1975	62.1	51,500
6	0.1973	53.9	44,700
7	0.1982	75.9	62,200
8	0.2028	61.8	47,300
9	0.1963	72.7	61,300
10	0.2005	72.3	57,300
11	0.1980	62.7	51,500
12	0.1991	67.6	54,600
13	0.1996	75.7	60,700
14	0.1971	69.5	57,900
15	0.1989	72.3	58,700
16	0.1972	80.8	67,200
17	0.1984	56.1	45,900
		Average Modulus of Rupture =	55,500
		Standard Deviation =	6,100

Table 12. Continued. h) 825°F. for 6 Hours Leaching.

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.2007	62.3	49,200
2	0.1973	57.9	48,100
3	0.1979	79.4	65,300
4	0.2027	68.3	52,300
5	0.1974	71.1	59,000
6	0.1972	64.6	53,700
7	0.2001	71.3	56,800
8	0.1965	67.4	56,700
9	0.1971	73.9	61,600
10	0.1998	64.1	51,200
11	0.1966	51.6	43,300
12	0.1971	66.7	55,600
13	0.1999	67.4	53,800
14	0.1978	68.5	56,400
15	0.2022	69.0	53,300
16	0.1991	66.0	53,400
17	0.1999	56.0	44,700
18	0.2017	73.9	57,500
		Average Modulus of Rupture =	54,000
		Standard Deviation =	5,400

Table 12. Continued. i) 825°F. for 8 Hours Leaching.

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1978	63.0	51,900
2	0.1970	62.8	52,400
3	0.2016	73.6	57,300
4	0.1997	54.9	44,000
5	0.1992	64.6	52,100
6	0.1982	45.4	37,200
7	0.2011	63.0	49,400
8	0.1998	77.6	62,100
9	0.2014	70.0	54,700
10	0.1990	60.4	48,900
11	0.1978	67.6	55,700
12	0.2028	61.1	46,700
13	0.1972	71.3	59,300
14	0.2014	80.8	63,100
15	0.2007	79.9	63,100
16	0.1999	71.3	56,900
17	0.1989	73.7	59,800
		Average Modulus of Rupture =	53,800
		Standard Deviation =	6,900

Table 12. Continued. j) 825°F. for 12 Hours Leaching.

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.2030	73.7	56,200
2	0.2005	62.5	49,500
3	0.1979	70.9	58,400
4	0.2034	72.7	55,100
5	0.2025	70.4	54,100
6	0.2024	74.4	57,300
7	0.1968	62.0	51,900
8	0.2017	53.0	41,200
9	0.1973	63.9	53,100
10	0.1984	68.5	55,900
11	0.2017	67.6	52,600
12	0.2056	63.2	46,500
13	0.1962	58.8	49,700
14	0.1989	68.1	55,200
15	0.2020	67.6	52,300
16	0.1998	61.8	49,400
17	0.1999	73.4	58,600
18	0.1995	67.8	54,500
19	0.2040	70.7	53,000
20	0.2021	80.8	62,400

Average Modulus of Rupture = 53,300

Standard Deviation = 4,600

Table 12. Continued. k) 1000°F. for 2 Hours Leaching

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1997	65.5	52,500
2	0.2001	58.8	46,800
3	0.1971	55.8	46,500
4	0.1976	43.6	36,100
5	0.1999	52.6	42,100
6	0.1992	49.3	46,800
7	0.1984	54.2	40,200
8	0.1982	51.2	44,400
9	0.1975	53.0	42,400
10	0.1991	57.7	51,000
11	0.2009	49.8	35,500
12	0.2008	64.1	36,300
13	0.2008	34.1	50,500
14	0.1987	34.1	27,800
15	0.1980	51.4	42,200
16	0.1980	60.1	49,400
17	0.2003	67.0	53,200
18	0.1985	51.0	41,600
19	0.1987	62.4	50,800
		Average Modulus of Rupture =	44,700
		Standard Deviation =	6,100

Table 12. Continued. 1) 1000°F. for 4 Hours Leaching

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.1979	37.7	31,100
2	0.2005	15.8	12,500
3	0.2037	52.9	39.900
4	0.1969	40.8	34,100
5	0.1967	37.9	31,800
6	0.1975	40.1	33,200
7	0.1963	44.2	37,300
8	0.2047	45.5	33,900
9	0.1976	43.7	36,200
10	0.2061	56.4	41,100
11	0.1966	30.1	25,300
12	0.1989	40.2	32,600
13	0.1965	37.8	31,800
14	0.1958	42.2	35,900
15	0.1984	34.4	26,500
16	0.1981	37.7	31,000
17	0.1958	38.2	32,400
18	0.1974	22.7	18,900
19			
		Average Modulus of Rupture =	31,400
		Standard Deviation =	6,800

Table 12. Continued. m) 1000°F. for 6 Hours Leaching

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.2001	21.9	17,400
2	0.2040	18.7	14,000
3	0.2003	18.6	14,400
4	0.2022	32.9	25,400
5	0.1980	22.6	18,600
6	0.1960	25.6	21,700
7	0.1979	24.6	20,200
8	0.2011	22.7	17,800
9	0.2030	24.1	18,400
10	0.2038	16.8	12,900
11	0.1997	10.5	8,400
12	0.2060	22.9	16,700
13	0.2047	24.6	18,300
14	0.1994	20.1	16,200
15	0.1977	59.2	19,800
16	0.1967	59.0	19,900
17	0.1992	27.0	21,800
18	0.1989	26.7	21,600
		Average Modulus of Rupture =	18,000
		Standard Deviation =	3,800

Table 12. Continued. n) 1000°F. for 8 Hours Leaching

Specimen Number	Diameter (Inches)	Load (lbs)	Modulus of Rupture (psi)
1	0.2021	29.5	22,800
2	0.1964	38.0	32,000
3	0.2019	40.3	31,200
4	0.1991	37.0	29,900
5	0.1964	34.8	29,400
6	0.1990	33.8	27,400
7	0.1999	32.3	25,800
8	0.1976	32.2	26,700
9	0.2008	40.3	31,700
10	0.2000	26.7	21,300
11	0.2030	30.2	23,000
12	0.2060	27.4	20,000
13	0.2010	19.4	15,300
14	0.2031	36.6	27,100
15	0.1984	31.6	25,800
16	0.1976	27.0	22,400
17	0.2011	25.3	19,900
18	0.1960	29.5	25,000
19	0.1998	32.1	25,700
20	0.2058	38.9	28,400
		Average Modulus of Rupture =	25,500
		Standard Deviation =	4,300

Table 13. Modulus of Rupture of Soda-Lime Glass Rods Leached in KNO_3 at 750°F. for 4 Hours

Rod Number	Load (Pounds)	Diameter (Inches)	Modulus of Rupture (Pounds Per Square Inch)
1	78.0	0.1998	49,800
2	73.8	0.1994	47,400
3	79.6	0.2001	50,600
4	109.0	0.2000	69,200
5	108.0	0.1981	70,400
6	92.9	0.1974	61,500
7	89.9	0.1958	61,000
8	80.9	0.1999	51,600
9	97.6	0.1969	65,100
10	77.3	0.1997	49,400
		Average Modulus of Rupture =	57,600
		Standard Deviation =	8,800

APPENDIX C

RESULTS FOR SODA-LIME GLASS LEACHED IN A VARIETY OF LITHIUM SALT BATHS

In addition to those lithium salt baths discussed in detail in the body of this paper, experimental work was done with several other salt baths. All of these baths caused severe surface attack of rods or posed other serious problems and are included here only for completeness.

An attempt was made to duplicate some diffusion studies summarized in a Russian paper (11). This paper described diffusion using a combination of lithium nitrate and potassium bisulfate ($KHSO_4$) as the molten salt bath. The Russians postulate that a series of decomposition reactions take place in the $KHSO_4$ on heating, releasing "superactive" water and acid sulfates capable of melting or dissolving the surface layer of glass. The siliceous surface layer does not mix with the molten salts after melting, and a "perfect" surface is formed between the two immiscible liquids. Thus surface attack is minimized, and in principle, the surface of the treated glass can actually be better than that of the untreated surface. Thus it is possible to expect a lithium-rich surface layer of substantial thickness to be quickly obtained, along with an improved glass surface after treatment.

According to the authors (11), the reactions proceed roughly as follows:

Since the introduction of additives occurs at a comparatively high temperature, the unstable bisulfates (e.g. of potassium) decompose immediately into pyrosulfate and water:

$$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O$$

Pyrosulfate is also unstable:

$$K_2S_2O_7 \rightarrow SO_3 + K_2SO_4$$

The double salt K_2SO_4 - $KHSO_4$, which later decomposes to potassium sulfate sulfurous gas, and water shows greater stability at the treatment temperature. The highly active water formed by these reactions can dissolve silica, i.e. cause cleavage of SiO bonds and transform silica from skeleton into molecular form.

The appearance of the silica hydrate and the presence of alkali-metal sulfates make feasible reactions which form silicates of lithium, sodium, and potassium. The initial temperature for these reactions is 1100 - 1200°C., but the presence of highly reactive water in the melt favors the formation of silicate in the temperature region of 580-600°C., corresponding to the softening of the glass:

$$(Me)_2SO_4 + H_2O + nSiO_2 \rightarrow (Me)_2O.nSiO_2 + H_2O + SO_3$$

A factor contributing to the feasibility of this reaction is the lithium silicate glass composition of the surface layer with a softening point that is 60° lower than the treatment temperature. This is actually highly viscous liquid.

Upon the interaction of silicates and sulfates of alkali metals, we observe the limited mutual solubility of these salts and as a consequence, the phenomenon of liquefaction. Two immixable liquids are formed which have an extremely small degree of surface tension, and a boundary which represents an ideal plane. The

> distribution that is valid for immixable liquids determines the normal diffusion process of sodium^{+1} from the glass and of lithium^{+1} into the glass.
>
> An additional result of these processes is that the surface defects disappear and the strength of the treated glass increases markedly.

Attempts to duplicate this work using $KHSO_4$ were made and this technique may very well warrant additional study; however, the formation of large quantities of SO_3 present serious problems. Not only is the gaseous form of SO_3 highly toxic, but the SO_3 also dissociates in water to form sulfuric acid (H_2SO_4) which makes containing the reaction extremely difficult. Considerable work was done without finding a safe way to carry out the experiment. As a laboratory curiosity, this technique is interesting, but it is doubtful that it could ever be incorporated into mass production facilities.

In addition to work done in trying to duplicate the Russian article described above, exchange was tried using several other lithium salts. Primarily, LiCl, alone and in combination with Na_2SO_4 or $NaNO_3$ was tested. In all cases, leaching soda-lime glass rods in these baths produced notable surface attack after only 5 minutes of leaching.

APPENDIX D

DETERMINATION OF STRENGTH FOR SODA-LIME GLASS RODS SPRAYED WITH KNO_3 AND HEAT TREATED

Sample groups of about twenty-five soda-lime glass rods were preheated to 300°F., sprayed with a saturated aqueous solution of potassium nitrate, and then heat treated at temperatures of 660°, 740°, 800°, 850°, and 1000°F., for times ranging from 15 minutes to 24 hours. The modulus of rupture was calculated for each rod and is presented in Table 14 along with the average modulus and standard deviation for the individual groups.

Table 14. Modulus of Rupture for Soda-Lime Glass Rods Sprayed With a Saturated Aqueous Solution of KNO_3 and Heat Treated at Al) 660° for 15 Minutes

Rod Number	Load	Diameter	Modulus of Rupture
1	40.0	0.1985	26,100
2	48.9	0.1990	31,700
3	42.1	0.1980	27,700
4	43.3	0.1995	27,800
5	39.1	0.1986	25,500
6	38.5	0.1974	25,600
7	56.8	0.1977	37,600
8	28.0	0.1982	18,300
9	41.5	0.1982	27,200
10	43.6	0.1991	28,200
11	26.4	0.1986	17,200
12	40.8	0.1991	26,400
13	47.5	0.1969	31,800
14	24.6	0.1986	16,100
15	37.1	0.1979	24,500
16	37.0	0.1981	24,300
17	54.4	0.1973	36,100
18	34.7	0.1980	22,800
19	36.6	0.2006	23,100
20	31.0	0.1975	20,500
21	43.6	0.1975	28,900
22	36.4	0.1965	24,500
23	48.9	0.1966	32,900
24	33.6	0.1994	21,600
25	33.4	0.1978	22,100

Average Modulus of Rupture = 25,500

Standard Deviation = 5,600

Table 14. Continued. A2) 660°F. for 30 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	32.2	0.1981	21,100
2	50.7	0.2023	31,300
3	38.2	0.1939	26,700
4	31.3	0.1935	22,100
5	54.7	0.1996	35,100
6	34.3	0.1989	22,300
7	27.1	0.1981	17,800
8	53.9	0.1982	35,300
9	43.1	0.1996	27,700
10	32.4	0.1982	21,200
11	52.3	0.1973	34,700
12	54.4	0.1983	35,600
13	48.9	0.1981	32,100
14	40.0	0.1976	26,400
15	47.9	0.2017	29,800
16	36.4	0.1971	24,300
17	32.4	0.1979	21,300
18	49.3	0.2020	30,500
19	40.5	0.1989	26,300
20	54.4	0.1992	35,100
21	46.3	0.1987	30,100
22	47.9	0.1972	31,900
23	39.6	0.1977	26,200
24	35.4	0.1981	23,200
25	43.6	0.1990	28,300
		Average Modulus of Rupture =	27,900
		Standard Deviation =	5,300

Table 14. Continued. A3) 660°F. for 1 Hour.

Rod Number	Load	Diameter	Modulus of Rupture
1	36.8	0.1938	25,800
2	51.9	0.2021	32,100
3	51.0	0.2029	31,200
4	46.1	0.1988	30,000
5	37.7	0.2029	23,000
6	45.8	0.1965	30,800
7	42.1	0.2006	26,600
8	44.4	0.1953	30,400
9	33.1	0.1972	22,000
10	36.8	0.1950	25,300
11	44.0	0.1975	29,200
12	35.0	0.1950	24,100
13	65.5	0.2004	41,500
14	39.4	0.1974	26,200
15	45.9	0.1970	30,700
16	34.3	0.1973	22,800
17	45.2	0.1999	28,900
18	44.4	0.1973	29,500
19	41.7	0.2003	26,500
20	49.5	0.1970	33,000
21	49.3	0.1960	33,400
22	46.8	0.1978	30,900
23	45.4	0.1969	30,400
		Average Modulus of Rupture =	28,900
		Standard Deviation =	4,300

Table 14. Continued. A4) 660°F. for 2 Hours

Rod Number	Load	Diameter	Modulus of Rupture
1	35.0	0.2015	21,900
2	35.4	0.2002	22,500
3	37.5	0.1963	25,300
4	41.5	0.2004	26,300
5	59.1	0.1992	38,200
6	42.1	0.1987	27,400
7	30.8	0.1986	20,100
8	41.7	0.1988	27,100
9	51.0	0.1955	34,900
10	52.3	0.1980	34,400
11	46.8	0.1987	30,500
12	40.3	0.2002	25,600
13	45.1	0.1995	29,000
14	37.7	0.1993	24,300
15	32.6	0.2004	20,700
16	38.4	0.1995	24,700
17	50.3	0.1992	32,500
18	32.9	0.1992	32,500
19	40.0	0.2006	25,300
20	51.0	0.2006	32,300
21	37.0	0.1996	23,700
22	57.2	0.2011	35,900
23	35.2	0.1989	22,800
24	48.2	0.1952	33,100
		Average Modulus of Rupture =	27,500
		Standard Deviation =	5,300

Table 14. Continued. A5) 660°F. for 4 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	69.5	0.1984	45,400
2	62.5	0.2022	8,600
3	50.7	0.1971	33,800
4	56.3	0.2008	35,500
5	43.8	0.1947	30,300
6	51.9	0.1946	36,000
7	46.3	0.1984	30,300
8	54.4	0.1957	37,000
9	42.9	0.1981	28,200
10	56.5	0.1981	37,100
11	73.4	0.1995	47,200
12	51.4	0.1989	33,300
13	56.1	0.1993	36,200
14	53.7	0.1978	35,400
15	40.8	0.1931	28,900
16	61.4	0.1983	40,200
17	57.2	0.1996	36,700
18	57.7	0.1999	36,900
19	41.0	0.1986	26,700
20	49.3	0.1990	31,900
21	50.7	0.19 0	33,800
22	50.9	0.1960	34,500
23	48.6	0.1961	32,900
24	51.0	0.1976	33,800
25			

Average Modulus of Rupture = 35,100

Standard Deviation = 4,800

Table 14. Continued. A6) 660°F. for 12 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	38.7	0.1975	25,700
2	32.2	0.2013	20,200
3	42.6	0.1971	28,400
4	42.8	0.1948	29,500
5	44.5	0.1965	30,000
6	42.8	0.1956	29,200
7	40.3	0.2011	25,300
8	41.9	0.1986	27,300
9	41.9	0.1956	28,600
10	55.3	0.2016	34,400
11	55.3	0.1956	37,700
12	66.7	0.1962	45,100
13	49.3	0.1966	33,100
14	33.6	0.1973	22,300
15	55.8	0.1983	36,500
16	47.7	0.1999	30,500
17	64.1	0.2016	39,900
18	84.5	0.1998	54,900
19	59.8	0.2001	38,100
20	82.7	0.1967	55,500
21	41.5	0.1985	27,100
22	57.7	0.2032	35,100
23	55.6	0.1989	36,100
24	68.3	0.2014	42,700
25	64.4	0.2004	40,900
		Average Modulus of Rupture =	34,200
		Standard Deviation =	8,900

Table 14. Continued. A7) 6 0°F. for 24 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	45.4	0.1973	30,200
2	58.8	0.2019	36,500
3	74.3	0.2005	47,000
4	67.8	0.2025	41,700
5	71.6	0.1998	45,800
6	43.6	0.1947	30,200
7	48.9	0.2011	30,700
8	44.7	0.1964	30,100
9	37.8	0.1989	24,500
10	111.9	0.1976	74,100
11	48.4	0.2004	30,700
12	84.5	0.1958	57,400
13	64.4	0.1977	42,600
14	61.8	0.1983	40,400
15	50.3	0.1944	35,000
16	54.4	0.1985	35,500
17	51.6	0.1943	35,900
18	85.7	0.1961	58,000
19	43.8	0.1956	29,900
20	50.5	0.1981	33,200
21	45.2	0.1995	29,100
22	41.2	0.1984	26,900
23	59.8	0.1981	39,300
24			
		Average Modulus of Rupture =	38,500
		Standard Deviation =	11,800

Table 14. Continued. B1) 740°F. for 15 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	33.1	0.1987	21,500
2	48.0	0.2006	30,400
3	53.7	0.2036	32,500
4	41.9	0.1965	28,200
5	45.8	0.2017	28,500
6	50.5	0.1970	33,700
7	55.3	0.1980	36,300
8	66.9	0.1996	42,900
9	35.4	0.1998	22,600
10	57.4	0.1960	38,900
11	43.8	0.2035	26,500
12	63.4	0.1980	41,700
13	35.7	0.1969	23,900
14	29.0	0.1995	18,700
15	68.6	0.2019	42,600
16	50.9	0.1970	34,000
17	46.3	0.1991	29,900
18	47.2	0.1968	31,600
19	39.1	0.1967	26,200
20	51.2	0.1952	35,100
21	53.9	0.1956	36,700
22	52.6	0.1987	34,200
23	28.9	0.1997	18,500
24	33.4	0.1980	25,200
		Average Modulus of Rupture =	30,800
		Standard Deviation =	7,100

Table 14. Continued. B2) 740°F. for 30 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	54.0	0.1958	36,700
2	52.1	0.2001	33,200
3	41.4	0.1974	27,400
4	61.6	0.2028	37,700
5	42.1	0.2028	25,700
6	45.1	0.2027	27,600
7	28.3	0.1962	19,200
8	44.0	0.2038	26,500
9	43.3	0.2031	26,400
10	58.3	0.1993	37,600
11	35.6	0.2005	22,500
12	47.2	0.1974	31,300
13	36.6	0.1997	23,500
14	63.2	0.1988	41,000
15	59.5	0.2020	36,800
16	55.3	0.1969	37,000
17	47.5	0.2020	29,400
18	67.9	0.1984	44,400
19	57.7	0.1974	38,300
20	50.0	0.1974	33,200
21	56.0	0.1985	36,500
22	59.7	0.2003	37,900
23	48.8	0.1994	31,400
24	53.0	0.1982	34,700
25	50.0	0.1997	32,000
		Average Modulus of Rupture =	31,900
		Standard Deviation =	6,900

Table 14. Continued. B3) 740°F. for 1 Hour.

Rod Number	Load	Diameter	Modulus of Rupture
1	68.5	0.1985	44,700
2	49.5	0.2003	31,400
3	68.6	0.1986	44,700
4	46.6	0.1982	30,600
5	38.7	0.1974	25,700
6	50.7	0.2033	30,800
7	54.2	0.2007	34,200
8	73.4	0.2019	45,500
9	40.5	0.1963	32,000
10	51.2	0.1978	33,800
11	54.7	0.2000	34,900
12	54.7	0.1975	36,300
13	35.4	0.2012	22,200
14	47.7	0.1977	31,500
15	65.8	0.1964	44,400
16	48.6	0.2001	30,900
17	41.2	0.1969	27,500
18	40.1	0.1975	26,600
19	73.7	0.1989	47,800
20	49.6	0.2022	30,600
21	56.3	0.2003	35,800
22	55.4	0.2011	34,800
23	56.1	0.2016	35,000
24	57.2	0.1964	38,500
25	64.2	0.2030	39,200
		Average Modulus of Rupture =	34,800
		Standard Deviation =	6,700

Table 14. Continued. B4) 740°F. for 2 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	61.6	0.1954	42,100
2	41.7	0.2000	26,600
3	57.6	0.2007	36,300
4	66.9	0.1967	44,900
5	37.5	0.2015	23,400
6	50.3	0.1967	33,800
7	42.8	0.1962	28,900
8	72.5	0.2024	44,600
9	88.0	0.1976	58,200
10	56.3	0.1974	37,400
11	51.9	0.1979	34,200
12	61.4	0.2008	38,700
13	52.4	0.1972	34,900
14	46.1	0.1963	31,100
15	70.2	0.2011	44,100
16	51.7	0.1987	33,700
17	72.7	0.1996	46,700
18	59.8	0.1954	40,900
19	35.2	0.1944	24,500
20	35.2	0.1977	23,300
21	74.4	0.1974	49,400
22	59.1	0.1965	39,800
23	66.4	0.2031	40,400
24	74.1	0.2004	47,000
		Average Modulus of Rupture =	37,700
		Standard Deviation =	8,800

Table 14. Continued. B5) 740°F. for 12 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	60.0	0.1995	38,600
2	67.1	0.2001	42,700
3	82.7	0.2008	52,200
4	37.0	0.1960	25,100
5	60.9	0.1998	39,000
6	54.0	0.1961	36,600
7	69.3	0.1958	47,200
8	66.7	0.1995	42,900
9	80.1	0.2020	49,600
10	74.6	0.1979	49,100
11	107.7	0.2000	68,700
12	73.0	0.1978	48,200
13	73.6	0.1981	48,300
14	46.5	0.1996	29,800
15	62.0	0.1995	39,800
16	35.4	0.1959	24,000
17	56.0	0.1975	47,100
18	98.4	0.1997	63,100
19	67.2	0.1996	43,200
20	44.9	0.1966	30,100
21	69.5	0.1998	44,500
22	52.6	0.1956	33,900
23	90.8	0.1991	58,700
24	49.8	0.2006	31,500
25	59.0	0.2013	36,900

Average Modulus of Rupture = 42,500

Standard Deviation = 11,000

Table 14. Continued. B6) 740°F. for 12 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	65.5	0.1990	42,400
2	65.3	0.2010	41,000
3	69.3	0.2010	43,600
4	41.5	0.2030	25,300
5	74.4	0.2017	46,300
6	63.5	0.1981	41,700
7	61.1	0.1983	40,000
8	65.1	0.2003	41,400
9	68.3	0.1994	44,000
10	100.5	0.1977	66,400
11	71.1	0.2110	44,700
12	65.6	0.1938	46,000
13	62.7	0.1984	41,000
14	41.4	0.1974	27,400
15	57.2	0.1959	38,800
16	68.5	0.1972	45,600
17	62.3	0.2013	39,000
18	61.6	0.1968	41,300
19	59.5	0.1971	39,700
20	79.2	0.1988	51,500
21	58.4	0.1975	38,700
22	62.1	0.1990	40,200
		Average Modulus of Rupture =	42,100
		Standard Deviation =	7,800

Table 14. Continued. B7) 740°F. for 24 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	73.0	0.1971	48,700
2	50.7	0.1963	34,200
3	74.1	0.1998	47,400
4	76.4	0.1960	51,800
5	57.4	0.1985	37,400
6	55.3	0.1980	36,300
7	59.7	0.1984	39,000
8	64.9	0.1960	44,000
9	58.6	0.2003	37,200
10	61.4	0.1986	40,000
11	66.2	0.1972	44,000
12	73.7	0.1988	47,900
13	50.9	0.1975	33,700
14	46.6	0.1988	30,300
15	44.4	0.1978	29,300
16	48.2	0.2012	30,200
17	80.1	0.1950	55,100
18	77.8	0.1989	50,500
19	70.0	0.1979	46,100
20	60.7	0.2000	38,700
21	50.3	0.1993	32,500
22	72.2	0.1971	48,100
23	57.4	0.1991	37,100
24	72.2	0.1980	47,500
25	64.4	0.2016	40,100
		Average Modulus of Rupture =	41,100
		Standard Deviation =	7,400

Table 14. Continued. C1) 800°F. for 15 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	43.5	0.1971	29,000
2	57.2	0.1976	37,800
3	33.4	0.2002	21,300
4	56.5	0.1980	37,200
5	48.9	0.1978	32,300
6	34.8	0.1996	22,400
7	53.5	0.2014	33,400
8	54.2	0.2018	33,700
9	45.4	0.1989	29,500
10	49.5	0.2007	31,200
11	45.9	0.1983	30,100
12	38.9	0.2028	23,800
13	50.9	0.1990	32,900
14	42.4	0.1955	29,000
15	47.7	0.1981	31,300
16	41.4	0.1985	27,000
17	57.7	0.1970	38,500
18	47.3	0.1950	32,600
19	41.2	0.2018	25,600
20	41.9	0.2003	26,600
21	54.4	0.1970	36,300
22	46.6	0.1981	30,600
23	52.8	0.2018	32,800
24	51.0	0.2015	31,800
25	47.5	0.1990	30,800
		Average Modulus of Rupture =	30,700
		Standard Deviation =	4,500

Table 14. Continued. C2) 800°F. for 30 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	47.7	0.1972	31,700
2	43.8	0.1974	29,100
3	35.0	0.2030	21,400
4	76.2	0.1936	53,600
5	57 4	0.1956	39,100
6	59.7	0.1987	38,800
7	26.9	0.2007	17,000
8	63.0	0.1967	42,300
9	51.6	0.2009	32,500
10	47.0	0.1954	32,200
11	47.3	0.2038	28,500
12	49.6	0.2013	31,100
13	68.6	0.1977	45,300
14	39.6	0.1994	25,500
15	34.0	0.1953	23,300
16	63.0	0.2019	39,100
17	45.1	0.1982	29,500
18	51.0	0.1990	33,100
19	40.8	0.1981	26,800
20	48.0	0.1970	32,100
21	59.8	0.2007	37,800
22	44.4	0.1958	30,200
		Average Modulus of Rupture =	32,700
		Standard Deviation =	8,300

Table 14. Continued. C3) 800°F. for 1 Hour.

Rod Number	Load	Diameter	Modulus of Rupture
1	49.5	0.2001	31,500
2	41.9	0.1947	29,000
3	64.2	0.1976	42,500
4	59.3	0.1966	39,800
5	84.5	0.1995	54,300
6	88.0	0.2037	53,100
7	46.1	0.1986	30,000
8	71.1	0.2009	44,800
9	66.7	0.2014	41,700
10	60.7	0.2000	48,700
11	73.4	0.2022	45,300
12	90.5	0.1990	58,600
13	54.6	0.1987	35,500
14	63.5	0.1965	42,700
15	43.5	0.2009	27,400
16	69.0	0.1968	46,200
17	41.5	0.1970	27,700
18	65.3	0.2026	40,100
19	63.4	0.1984	41,400
20	43.1	0.1964	29,100
21	54.6	0.1990	35,300
22	68.8	0.1993	44,400
23	40.5	0.1980	26,600
		Average Modulus of Rupture =	39,400
		Standard Deviation =	9,000

Table 14. Continued. C4) 800°F. for 2 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	72.0	0.1966	48,400
2	43.3	0.2012	27,100
3	67.1	0.1969	44,800
4	64.8	0.2016	40,300
5	62.5	0.1986	40,700
6	52.1	0.1984	34,100
7	47.2	0.1981	31,000
8	62.3	0.1994	40,100
9	38.4	0.1993	24,700
10	67.1	0.1971	44,700
11	49.3	0.1991	31,900
12	69.0	0.1970	46,100
13	57.6	0.1984	37,600
14	50.3	0.1956	34,300
15	76.9	0.1996	49,400
16	78.0	0.1986	50,800
17	44.5	0.2030	27,200
18	66.9	0.2019	41,500
19	57.7	0.2001	36,800
20	52.8	0.1960	35,800
21	57.9	0.1991	37,400
22	63.2	0.1976	41,800
23	77.3	0.2039	46,500
24	45.9	0.1948	31,700
25	65.5	0.1958	44,500
		Average Modulus of Rupture =	38,800
		Standard Deviation =	7,300

Table 14. Continued. C5) 800°F. for 4 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	37.8	0.1980	24,900
2	66.2	0.1987	43,100
3	48.8	0.1955	33,300
4	49.3	0.1963	33,300
5	47.7	0.2000	30,400
6	27.8	0.1986	18,100
7	35.2	0.1990	22,800
8	36.6	0.1977	24,200
9	61.4	0.1978	40,500
10	74.3	0.2018	46,100
11	51.0	0.1998	32,700
12	33.8	0.1992	21,800
13	65.6	0.1984	42,900
14	43.6	0.1954	29,900
15	49.1	0.1986	32,000
16	67.2	0.2035	40,700
17	44.2	0.2017	27,500
18	51.7	0.1971	34,500
19	60.7	0.1989	39,400
20	51.4	0.2005	32,500
21	51.6	0.2022	31,800
22	61.2	0.2019	38,000
23	50.9	0.1995	32,700
24	28.9	0.1995	18,600
25	41.2	0.2001	26,200
		Average Modulus of Rupture =	31,900
		Standard Deviation =	7,700

Table 14. Continued. C6) 800°F. for 12 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	41.7	0.1985	27,200
2	46.3	0.2030	28,200
3	32.0	0.1956	21,800
4	31.9	0.1999	20,400
5	45.8	0.2000	29,200
6	44.2	0.1972	29,400
7	50.7	0.2015	31,600
8	44.0	0.1995	28,300
9	29.9	0.2000	19,100
10	43.5	0.1985	28,400
11	33.8	0.1966	22,700
12	44.7	0.1988	28,600
13	46.6	0.1961	31,600
14	50.2	0.1989	32,500
15	37.7	0.1964	25,400
16	41.4	0.1976	27,400
17	29.2	0.2001	18,600
18	42.4	0.1955	29,000
19	54.7	0.1987	35,600
20	55.4	0.1997	35,500
21	51.0	0.1967	34,200
22	54.7	0.1958	37,200
23	46.6	0.1978	30,800
24	60.7	0.2035	36,800
25	51.2	0.2033	31,100
		Average Modulus of Rupture =	28,800
		Standard Deviation =	5,300

Table 14. Continued. C7) 800°F. for 24 Hours

Rod Number	Load	Diameter	Modulus of Rupture
1	37.8	0.1972	25,200
2	41.9	0.1974	27,800
3	31.7	0.1974	21,000
4	38.5	0.2039	23,200
5	38.9	0.1969	26,000
6	46.1	0.2019	28,600
7	38.2	0.1957	26,000
8	48.4	0.2018	30,100
9	41.4	0.2037	25,000
10	42.9	0.1994	27,600
11	39.1	0.1994	25,200
12	40.5	0.1995	26,000
13	49.5	0.1970	33,000
14	55.6	0.1984	36,400
15	45.1	0.1987	29,300
16	34.7	0.2017	21,600
17	44.2	0.1961	29,900
18	51.6	0.1978	34,000
19	48.2	0.2000	30,800
20	37.5	0.1977	24,800
21	43.6	0.1990	28,300
22	24.5	0.2007	15,400
23	44.2	0.1982	29,000
24	49.5	0.1976	32,700
25	43.6	0.1974	29,000
		Average Modulus of Rupture =	27,400
		Standard Deviation =	4,500

Table 14. Continued. D1) 850°F. for 15 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	90.6	0.2010	57,000
2	73.0	0.1978	48,200
3	52.4	0.1976	34,700
4	67.8	0.2016	42,200
5	47.7	0.1984	31,200
6	57.4	0.1984	37,500
7	40.1	0.1974	26,600
8	54.0	0.1998	34,600
9	91.2	0.2018	56,600
10	52.8	0.2008	33,300
11	64.1	0.1987	41,700
12	46.3	0.2022	28,600
13	53.3	0.2016	33,200
14	60.4	0.1944	41,900
15	63.2	0.1946	43,800
16	35.2	0.1983	23,000
17	72.9	0.1961	49,300
18	49.6	0.2015	31,000
19	50.7	0.1984	33,100
20	80.3	0.1950	55,200
		Average Modulus of Rupture =	39,100
		Standard Deviation =	10,000

Table 14. Continued. D2) 850°F. for 30 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	44.0	0.2009	27,700
2	45.1	0.2015	28,100
3	72.2	0.2011	45,300
4	40.8	0.1992	26,400
5	45.1	0.2021	27,900
6	61.6	0.2000	39,300
7	57.6	0.1994	37,100
8	50.3	0.2015	31,400
9	58.4	0.1967	39,200
10	50.5	0.2009	31,800
11	58.4	0.1988	38,000
12	51.2	0.1953	35,100
13	64.8	0.1960	43,900
14	60.4	0.2038	36,400
15	54.7	0.2007	34,600
16	50.3	0.2006	31,800
17	63.0	0.1968	42,200
18	69.9	0.2018	43,400
19	63.2	0.1971	42,100
20	62.5	0.1971	41,700
21	58.3	0.1978	38,400
22	56.1	0.1976	37,100
23	52.4	0.2018	32,600
24	51.0	0.1951	35,100
25	58.1	0.1968	38,900
		Average Modulus of Rupture =	36,200
		Standard Deviation =	5,500

Table 14. Continued. D3) 850°F. for 1 Hour.

Rod Number	Load	Diameter	Modulus of Rupture
1(3)	59.0	0.1987	38,400
2(4)	53.5	0.2000	34,100
3(5)	43.8	0.1972	29,200
4(6)	61.1	0.1983	40,000
5(7)	45.6	0.1978	30,100
6(8)	66.7	0.1997	42,800
7(9)	79.4	0.2019	49,200
8(10)	68.6	0.1991	44,400
9(11)	37.8	0.1988	24,600
10(12)	48.4	0.1961	32,800
11(13)	35.0	0.1982	23,000
12(14)	58.6	0.1980	38,500
13(15)	65.8	0.2004	41,700
14(17)	66.0	0.1980	43,400
15(18)	49.3	0.1983	32,300
16(19)	54.4	0.1996	34,900
17(20)	45.2	0.1980	29,700
18(22)	57.2	0.1988	37,200
		Average Modulus of Rupture =	35,900
		Standard Deviation =	7,100

Table 14. Continued. D4) 850°F. for 2 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	63.0	0.1979	41,500
2	61.1	0.2017	38,000
3	61.4	0.2019	38,100
4	39.4	0.1980	25,900
5	59.3	0.1980	39,000
6	54.6	0.1970	37,000
7	35.9	0.1969	24,000
8	52.8	0.1955	36,100
9	50.7	0.1960	34,400
10	61.6	0.2019	38,200
11	55.1	0.1975	36,500
12	56.0	0.1974	37,100
13	46.8	0.2021	28,900
14	45.9	0.1980	30,200
15	43.6	0.1980	28,700
16	59.7	0.1999	38,100
17	67.9	0.1981	44,600
18	51.7	0.1983	33,900
19	29.7	0.1984	19,400
20	49.8	0.1987	32,400
21	44.2	0.1961	29,900
22	59.1	0.1979	39,900
23	61.4	0.1947	42,500
24	62.0	0.1930	44,000
25	54.0	0.1993	34,800
		Average Modulus of Rupture =	34,900
		Standard Deviation =	6,200

Table 14. Continued. D5) 850°F. for 4 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	61.2	0.1988	39,800
2	41.5	0.2030	25,300
3	44.0	0.1994	28,300
4	42.9	0.1985	28,000
5	49.6	0.2003	31,500
6	50.9	0.2034	30,900
7	53.7	0.1985	35,000
8	57.2	0.1983	37,400
9	56.1	0.2006	35,500
10	59.3	0.1971	39,500
11	44.2	0.1969	29,500
12	60.2	0.1989	39,000
13	44.9	0.1954	30,700
14	48.9	0.1975	32,400
15	50.7	0.1949	34,900
16	53.7	0.1984	35,100
17	58.8	0.2006	37,200
18	57.6	0.1947	39,800
19	34.7	0.1979	22,800
20	45.8	0.1950	31,500
21	44.0	0.1983	27,200
22	45.9	0.1953	31,500
23	47.7	0.1948	32,900
24	44.7	0.1941	31,200
25	60.0	0.2026	36,800
		Average Modulus of Rupture =	32,900
		Standard Deviation =	4,600

Table 14. Continued. D6) 850°F. for 12 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	56.0	0.1993	36,100
2	29.6	0.1966	19,900
3	48.8	0.2011	30,600
4	41.7	0.2026	25,600
5	40.7	0.1944	26,600
6	39.1	0.1986	25,500
7	43.1	0.1954	29,500
8	41.7	0.1999	26,700
9	37.7	0.1961	25,500
10	41.4	0.1958	28,100
11	54.0	0.1970	36,100
12	46.1	0.2002	29,300
13	34.1	0.1969	22,800
14	46.8	0.1990	30,300
15	37.5	0.1966	25,200
16	51.9	0.2029	31,700
17	36.8	0.1987	23,900
18	40.3	0.1981	26,500
19	38.7	0.2001	24,700
20	37.8	0.1973	25,100
21	35.7	0.2022	22,100
22	34.5	0.2006	21,800
23	57.2	0.2007	36,100
24	36.4	0.1960	24,700
		Average Modulus of Rupture =	27,300
		Standard Deviation =	4,500

Table 14. Continued. D7) 850°F. for 24 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	35.2	0.1973	23,400
2	40.8	0.1963	27,600
3	34.0	0.2000	21,700
4	32.4	0.1977	21,400
5	32.7	0.1962	22,100
6	33.4	0.1974	22,200
7	38.4	0.1950	26,400
8	39.4	0.2028	24,100
9	35.2	0.2015	22,000
10	35.2	0.1971	23,500
11	38.2	0.1969	25,500
12	28.3	0.1981	18,600
13	39.8	0.2023	24,500
14	40.0	0.1970	27,700
15	47.7	0.2005	30,200
16	45.4	0.2002	28,900
17	40.3	0.2006	24,400
18	37.0	0.1977	24,400
19	32.6	0.1980	21,400
20	32.6	0.1958	22,100
21	37.7	0.1996	24,200
22	47.7	0.1988	31,000
23	35.0	0.1977	23,100
24	35.6	0.1960	24,100
25	29.6	0.2006	25,100
		Average Modulus of Rupture =	24,300
		Standard Deviation =	2,900

Table 14. Continued. E1) 1000°F. for 15 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	36.6	0.1970	24,400
2	32.2	0.1970	31,500
3	38.5	0.2000	24,600
4	31.3	0.1987	20,400
5	54.6	0.1985	35,600
6	32.9	0.1967	22,100
7	51.9	0.1944	36,100
8	44.4	0.1991	28,700
9	32.4	0.1952	22,200
10	54.6	0.1976	36,100
11	39.2	0.2008	24,700
12	42.1	0.2016	26,200
13	37.0	0.1974	24,500
14	42.9	0.2020	26,600
15	37.8	0.2000	24,100
16	48.6	0.1987	31,600
17	39.8	0.2016	24,800
18	37.8	0.1989	24,500
19	35.2	0.2029	21,500
20	35.2	0.1987	22,900
21	43.5	0.2015	27,100
22	32.6	0.1942	22,700
23	56.3	0.1981	37,000
24	32.6	0.1974	21,600
25	58.6	0.2002	37,300
		Average Modulus of Rupture =	26,800
		Standard Deviation =	5,500

Table 14. Continued. E2) 1000°F. for 30 Minutes.

Rod Number	Load	Diameter	Modulus of Rupture
1	26.2	0.1982	17,200
2	31.3	0.1983	20,500
3	39.2	0.1971	26,200
4	33.6	0.1982	22,000
5	43.1	0.1978	28,400
6	42.9	0.1978	28,300
7	43.5	0.1972	28,900
8	33.4	0.1975	22,200
9	31.5	0.2015	19,700
10	33.4	0.1962	22,600
11	40.3	0.1998	25,800
12	23.4	0.2001	14,900
13	44.9	0.1997	28,800
14	40.8	0.2005	25,900
15	40.0	0.1987	26,000
16	34.7	0.2017	21,600
17	31.5	0.1996	20,200
18	26.6	0.1991	17,200
19	41.9	0.1980	27,500
20	33.4	0.1934	23,600
21	42.9	0.1993	27,700
22	43.5	0.1967	29,200
23	35.9	0.1997	23,000
24	33.4	0.1965	22,500
25	40.5	0.1991	26,200
		Average Modulus of Rupture =	23,800
		Standard Deviation =	4,100

Table 14. Continued. E3) 1000°F. for 1 Hour.

Rod Number	Load	Diameter	Modulus of Rupture
1	52.8	0.2018	32,800
2	33.3	0.1981	21,800
3	43.8	0.1941	30,600
4	40.5	0.1997	25,900
5	44.0	0.1974	29,200
6	45.1	0.1967	30,200
7	35.2	0.1994	22,700
8	49.1	0.2021	30,400
9	35.2	0.1981	23,100
10	41.9	0.1998	26,900
11	37.0	0.1971	24,600
12	41.0	0.1959	27,800
13	40.5	0.1974	27,900
14	36.6	0.1960	24,800
15	51.9	0.1984	33,900
16	36.3	0.2017	22,600
17	44.0	0.1989	28,500
18	33.1	0.1972	22,000
19	30.3	0.1958	20,600
20	35.4	0.1978	23,300
21	39.4	0.1981	25,900
22	25.5	0.1975	16,900
23	33.4	0.1991	21,600
24	32.0	0.1975	21,200
25	44.2	0.2000	28,200
		Average Modulus of Rupture =	25,700
		Standard Deviation =	4,200

Table 14. Continued. E4) 1000°F. for 2 Hours.

Rod Number	Load	Diameter	Modulus of Rupture
1	26.2	0.2023	16,200
2	34.8	0.1993	22,500
3	42.9	0.1995	27,600
4	23.8	0.1994	15,300
5	33.1	0.1985	21,600
6	40.0	0.2012	25,000
7	21.3	0.2018	13,200
8	28.3	0.1999	18,100
9	27.8	0.1998	17,800
10	35.2	0.1959	23,900
11	37.3	0.1990	24,200
12	28.5	0.1980	18,700
13	25.5	0.1986	16,600
14	35.2	0.1990	22,800
15	45.8	0.1976	30,300
16	33.6	0.1976	22,200
17	38.9	0.1956	26,500
18	28.0	0.1963	18,900
19	35.7	0.1951	24,600
20	26.6	0.2030	16,200
21	26.2	0.1983	17,200
22	23.2	0.2031	14,200
23	39.8	0.1974	26,400
24	26.8	0.1984	17,500
25	40.7	0.2018	25,300
		Average Modulus of Rupture =	20,900
		Standard Deviation =	4,700

APPENDIX E

DETERMINATION OF STRENGTH FOR SODA-LIME GLASS RODS, ACID ETCHED, SPRAYED WITH KNO_3, HEAT TREATED, AND ABRADED

A group of soda-lime glass rods was etched in a hydrofluoric - sulfuric acid solution for 30 seconds. Half the rods were heat treated to 550°F., sprayed with a saturated aqueous solution of KNO_3, and heat treated at 750°F. for 4 hours. Modulus of rupture values were determined for both treated and untreated rods, with and without surface abrasion. This data is included in Table 15 along with the average modulus of rupture and standard deviation for each group.

Table 15. Modulus of Rupture Values for Acid-Etched Soda-Lime Glass Rods Treated with KNO_3 at 750°F. for 4 Hours and Abraded.

(a) Etched in HF for 30 seconds

Rod Number	Load (Pounds)	Diameter (Inches)	Modulus of Rupture (psi)
1	48.2	0.1950	33,200
2	45.1	0.1925	32,200
3	47.9	0.1945	33,200
4	51.0	0.1921	36,800
5	55.6	0.1930	39,500
		Average Modulus of Rupture =	35,000
		Standard Deviation =	3,100

(b) Etch, Abraded with 120 Grit SiC

1	22.7	0.1942	15,800
2	23.8	0.1897	17,800
3	23.6	0.1895	17,700
4	23.8	0.1946	16,500
5	21.6	0.1922	15,600
		Average Modulus of Rupture =	16,700
		Standard Deviation =	1,000

(c) Etch, KNO_3 Spray, Treat 2 Hours at 750°F.

1	73.9	0.1886	56,200
2	57.2	0.1925	40,900
3	64.8	0.1905	47,800
4	64.6	0.1970	43,100
5	77.4	0.1930	55,000
		Average Modulus of Rupture =	48,600
		Standard Deviation =	6,900

Table 15. Continued.

(d) Etch, Heat Treat, Abraded

Rod Number	Load (Pounds)	Diameter (Inches)	Modulus of Rupture (psi)
1	23.4	0.1931	16,900
2	19.9	0.1930	14,100
3	23.1	0.1943	16,000
4	23.6	0.1940	16,500
5	19.9	0.1916	14,400
		Average Modulus of Rupture =	15,600
		Standard Deviation =	1,300

APPENDIX F

DETERMINATION OF THEORETICAL DEPTH OF DIFFUSION

In order to determine the maximum depth of diffusion for rods sprayed with KNO_3 and to serve as a check for the data obtained on these rods using flame photometry, calculations were made to find the number of potassium^{+1} ions available in the sprayed coating and the maximum depth for which they could replace all the Na^{+1} ions in the glass. In doing this, several important assumptions were made. It was assumed that (1) the sodium^{+1} content was homogeneous throughout the rod; (2) complete exchange of sodium^{+1} for potassium^{+1} took place; and (3) the interior limit of diffusion into the rod was at a fixed boundary plane.

From the literature, the density (ρ) for Kimble (Type R-6) glass was found to be 2.53 grams per cubic centimeter. Knowing this, the moles of Na^{+1} per cubic centimeter was calculated using equation (1):

$$\frac{\text{Moles } Na^+}{cm^3 \text{ glass}} = \frac{(2.53 \frac{gms}{cc})(15.5\% Na_2O)(\frac{2 \times 22.997 \text{ gms } Na^+}{61.979 \text{ gms } Na_2O})}{(22.997 \text{ gm Na/mole})}$$

$$= 0.0127 \frac{\text{moles } Na^+}{cc \text{ glass}} \qquad (1)$$

A rod was weighed before and after spraying and the weight of KNO_3 adhering was 0.1164 grams. This was used in equation (2) to find the moles of available K^{+1}:

$$\text{Moles of Available } K^+ = \frac{(0.1164 \text{ gms } KNO_3)(\frac{39.1 \text{ gms } K^+}{101.1 \text{ gms } KNO_3})}{(39.1 \frac{\text{gms } K^+}{\text{mole } K^+})}$$

$$= 0.00115 \text{ moles } K^+ \qquad (2)$$

The volume required for total replacement of Na^{+1} ions by available K^{+1} ions was determined in equation (3) by dividing the moles of available K^{+1} by the moles of Na^{+1} in the glass per cubic centimeter.

$$\text{Volume of Diffusion} = (\frac{0.00115 \text{ moles } K^+ \text{ available}}{0.0127 \frac{\text{moles } Na^+}{cc}})(0.0610 \frac{in^3}{cc})$$

$$= 0.00552 \text{ in}^3 \qquad (3)$$

Knowing the total volume required, equation (4) was used to determine the diameter of interior diffusion boundary.

$$\text{Volume of Diffusion} = \pi h(\frac{d_o}{2})^2 - \pi h(\frac{d_1}{2})^2$$

$$d_1 = 0.196 \text{ in.} \qquad (4)$$

where:

h = length of sprayed rod (in)

d_o = outside diameter of rod (in)

d_1 = diameter of interior diffusion boundary (in).

Finally this was used in equation (5) to determine the thickness of the layer of diffusion:

$$\frac{(d_o - d_1)}{2} \times \left(\frac{1000 \text{ mils}}{\text{in}}\right) \times \left(\frac{25.4 \text{ microns}}{\text{mil}}\right) = 40.6 \text{ microns} \qquad (5)$$

Thus for the average amount of KNO_3 deposited on the surface of a glass rod, it would be possible to obtain complete exchange down through approximately 41 microns. Partial exchange could theoretically take place through a much thicker layer.

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